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CONTENTS

		PAGE
66.	Studies in sulphonamides—A new approach. Part I.—By D. R. Shridhar and K. S. Narang	305
67.	Synthesis of a completely reduced analogue of hexestrol. 1:2-Diethyl-1-(4 - methoxy*cyclo*hexyl) - 2 - (4 - *iso*amyl*cyclo*hexyl) - ethane. — By (Miss) Sindhu Parkhi	313
68.	Studies in Fries migration. Part XIV. The Fries isomerisation of acyl esters of *o*- and *p*-hydroxyacetophenones and *p*-hydroxybenzophenone.—By M. R. Bhatt and N. M. Shah	318
69.	Setting of the gels of sodium oleate and stearate in some organic solvents. Part I. Time and temperature of setting.—By K. B. Deshpande and K. P. Buch ...	321
70.	Interaction of thionyl chloride and aromatic hydroxyketones in presence of finely divided copper. Part VIII. Preparation of 3:3′-dibutyryl-4:6-4′:6′-tetrahydroxy-diphenyl thioether and its derivatives from resbutyrophenone.—By V. J. Dalvi and G. V. Jadhav	323
71.	Possible antiamoebic agents: Mannich bases from 8-hydroxyquinolines.—By A. B. Sen and Yashwant D. Kulkarni	326
72	The use of some thioglycollanilides in inorganic analysis. Part II.—By R. C. Swain, R. N. Misra and S. S. Guha Sircar	329
73.	Colorimetric estimation of iron by diphenylthiovioluric acid.—By Lal C. Malik and R. P. Singh	335
74.	Experiments on the syntheses of furano compounds. Part VII. 1:2-benzodiphenylene oxide.—By J. N. Chatterjea	339
75.	Setting of the gels of sodium oleate and stearate in some organic solvents. Part II. Cooling curves of soap-solvent systems.—By K. B. Deshpande and K. P. Buch	346
76.	A note on the occurrence of "Ceryl alcohol" on *Argemoae mexicana*.—By Brojeswar Mazumder, Sachindra Nath Sarkar and Phanindra Chandra Dutta	351
77.	A note on bromination of oxymethylene ketones through their copper salts.—By H. C. Garg, Y. Singh and M. M. Bokadia	353
78.	A note on the oxidation of red phosphorus by potassium chlorate.—By G. S. Deshmukh and M. Venugopalan	355
79.	A note on component fatty acids of the oil from the seeds of *Momordica charantia*, Linn.—By J. P. Verma and J. S. Aggarwal	357
80.	A note on the structure of disulphoxides.—By B. N. Trivedi	359
81.	A note on solubility of hydrated copper oxide in nitric acid.—By S. C. Sircar and B. Prasad	361
	Review	363
	Obituary	365

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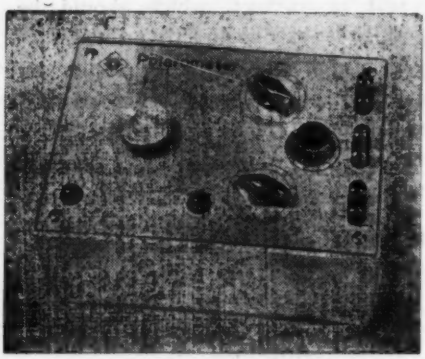

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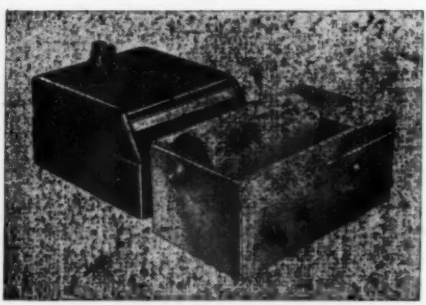

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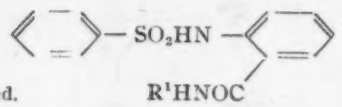
[Jour. Indian Chem. Soc., Vol. 33, No. 5, 1956]

STUDIES IN SULPHONAMIDES—A NEW APPROACH. PART I

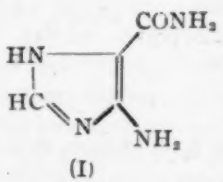
By D. R. Shridhar and K. S. Narang

Some sulphonamides of the general type



have been prepared and their properties described.

Amongst the sulphonamides sulphathiazole and sulphadiazine are the drugs of choice. Stetten and Fox (*J. Biol. Chem.*, 1945, **161**, 333) and Shive *et al.* (*J. Amer. Chem. Soc.*, 1947, **69**, 725) have established that these two sulphonamides interfere with the growth of bacteria, and 4-amino-5-carboxamido-imidazole (I) accumulates in the medium. Though it is well recognised that sulphonamides are bacteriostatic, it is not possible yet to draw a sharp line between a true bacteriostatic and a true bacteriocidal drug. Whether the imidazole (I) appears as a result of bacteriostatic or bacteriocidal nature, however small it may be, remains to be decided. However, it is obvious that these drugs act as antimetabolites to two essential metabolites, viz., *p*-aminobenzoic acid and 4-amino-5-carboxamido-imidazole.

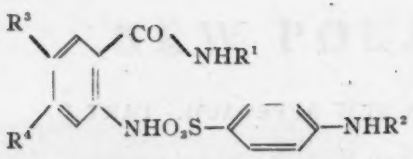


(I)

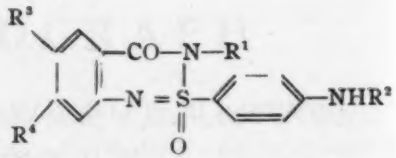
From the point of view of metabolite-antimetabolite relationship, there is no similarity between the structures of sulphathiazole and sulphadiazine with (I), and it may be concluded that their antimetabolite action with respect to (I) may be of a low order.

It is therefore considered of interest to synthesise new sulphonamides with combination of groups which possibly could act as antimetabolites against PABA as well as against (I) to a greater measure than is the case with the present known drugs of the class.

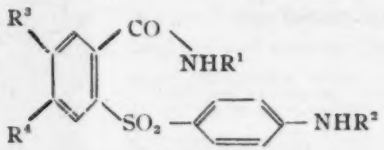
After surveying the subject of metabolites, particularly reviews by Roblin (*Chem. Rev.*, 1946, **38**, 255) and Wooley ("A Study of Antimetabolites", 1952, Chap. 10), it is considered worthwhile to synthesise compounds of the general structure (II), its ring-closed compound (IIA) and its corresponding sulphone (IIB). The work could be extended to compounds of the structures (III), (IV), (V) and (VI) and their corresponding ring-closed compounds and sulphones ; R^1, R^2, R^3, R^4 being H or other groups.



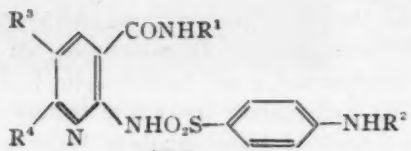
(II)



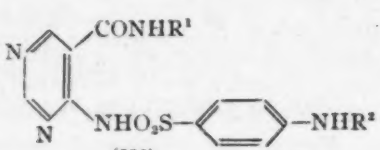
(IIA)



(IIB)



(III)



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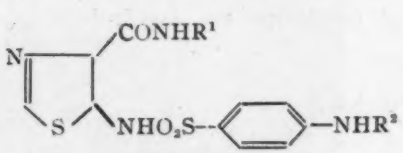

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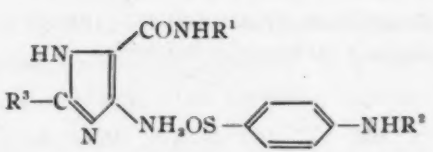
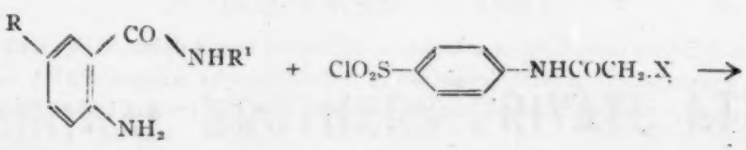


(VI)

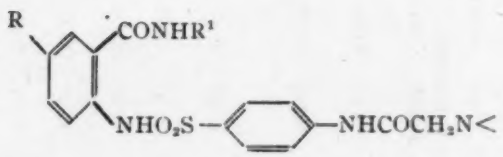
Besides the chemotherapeutic point of view, there is a fundamental interest involved in studying the chemistry of the rings (IIA) and the corresponding ring systems of (III), (IV), (V) and (VI), which will be new.

In the present investigation sulphonamides of the general structure (II) have been synthesised according to the following schemes:



(VII)

(VIII)



[R = H or Me ; R^1 = H or alkyl or thiazole or aryl group ; X = H or Cl]

EXPERIMENTAL

Formation of Amides.—A mixture of isatoic or 5-methylisatoic anhydride (1 *M*) (Bredt and Hof, *Ber.*, 1900, **33**, 27) and the particular amine (1 *M*) was heated on a water-bath for 2 hours and the compound crystallised from a suitable solvent. In case of the condensation with 2-amino-4-phenylthiazole, 2-amino-4-(*p*-chlorophenyl)-thiazole and 2-amino-4-methyl-5-carbethoxythiazole, the reaction temperatures used were 140°-160°, 160°-170° and 155°-165° respectively and the time allowed was only one hour in case of compounds No. 5, 12 and 13 (Table I).

Formation of Sulphonamides.—The various listed sulphonamides (Table II) have been prepared by one of the following two general methods.

Method A.—*o*-Aminobenzamide or substituted benzamide (1 *M*) was dissolved in a requisite amount of dry ether, and pyridine (1 *M*) was added to it. *p*-Acetylamino-benzenesulphonyl chloride (1 *M*) was mixed with it with shaking and allowed to stay for a requisite interval of time. In case there was no separation, the reaction mixture was gently refluxed for sometime. Ether was then removed and the residue triturated with hot water, cooled, filtered at suction and the substance crystallised.

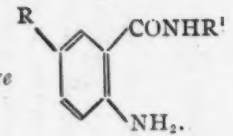
Method B.—*o*-Aminobenzamide or substituted benzamide (1 *M*) was mixed with pyridine (1 *M*), and *p*-acetylaminobenzenesulphonyl chloride (1 *M*) added and heated on a water-bath (or at 110-120° in some cases) for 2 hours. Pyridine hydrochloride was dissolved out with water as in method A and the residue was crystallised.

2-N^4-*Chloroacetylsulphanilamidobenzamide* (VIII : R = R^1 = H ; X = Cl).—This was prepared by method A using 120 c.c. of dry ether, pyridine (0.6 c.c.) for 1 g. of the 2-aminobenzamide, followed by the addition of *p*-chloroacetylaminobenzenesulphonyl chloride (1.97 g.). The resulting solution was warmed for 15 minutes and kept at room temperature for 50 hours. The residue after distillation of ether was treated with water (20 c.c.), collected and crystallised from 60% ethanol in white needles, m.p. 193°, yield 1.68 g. (Found : N, 11.80. $C_{15}H_{14}O_4N_3SCl$ requires N, 11.43 per cent).

2-N^4 - *Diethylaminoacetylsulphanilamide.*—To a solution of (VIII : R = R^1 = H ; X = Cl) (1 g.) in 15 c.c. of dry acetone was added diethylamine (2 *M*). After refluxing for one hour the solvent was distilled off and the residue washed with water (20 c.c.). The water-insoluble product was crystallised from ethanol in white needles, m.p. 200°, yield 0.45 g. (Found : N, 14.20. $C_{19}H_{24}O_4N_4S$ requires N, 13.86 per cent).

TABLE I

Amides of structure



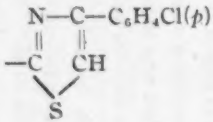
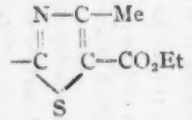
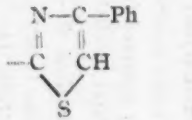
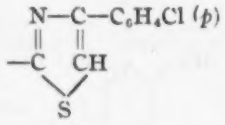
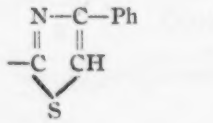
No.	Reactants. Anhydride.	Base	Product synthesised. Structure. R=	R₁=	Nomenclature.	Crvst. from.	M.P.	*Yield.	% Nitrogen. Found.	Calc.
1.	Isatoic	Ethanolamine	H	$-CH_2CH_2OH$	2-Amino- (-hydroxyethyl)-benzamide.	Benzene	95°	0.80 g.	16.10	15.60
2.	Do	*o*-Anisidine	H	$-C_6H_4OMe$ (*o*)	2-Aminobenz-*o*-anisidide.	66% EtOH	110°	2.06	11.50	11.57
3.	Do	2-Amino-4-(*p*-chlorophenyl)-thiazole	H		2-(2-Aminobenzamido)-4-(*p*-chlorophenyl)-thiazole.	EtOH	182°	1 95	12.60	12.74
4.	Do	2-Amino-4-methyl-5-carbethoxythiazole	H		2-(2-Aminobenzamido)-4-methyl-5-carbethoxy-thiazole.	Glacial acetic acid	138°	1.48	13.20	13.12
5.	Do	2-Amino-4-phenyl-thiazole	H		2-(2-Aminobenzamido)-4-phenylthiazole.	EtOH	150°	1.80	14.40	14.29

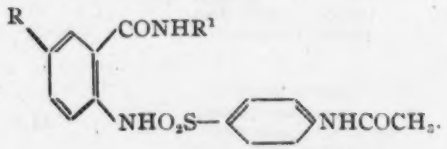
TABLE I (*contd.*)

No.	Reactants. Anhydride.	Base.	Product synthesised. Structure. R=	R_1=	Nomenclature.	Cryst. from.	M. P.	*Yield.	%Nitrogen. Found.	Calc.
6.	5-Methyl-isatoic	Aniline	Me	Ph	2-Amino-5-methylbenz-anilide.	EtOH	162°	1.70 g.	12.10	12 39
7.	Do	*o*-Toluidine	Me	—*o*-tol.	2-Amino-5-methylbenz-*o*-toluidide.	Aq. EtOH	170°	1.07	11.40	11.66
8.	Do	*m*-Toluidine	Me	—*m*-tol.	2-Amino-5-methylbenz-*m*-toluidide.	EtOH	148°	1.88	11.81	11.66
9.	Do	*p*-Toluidine	Me	—*p*-tol.	2-Amino-5-methylbenz-*p*-toluidide.	,,	183°	1.55	12.00	11.66
10.	Do	*o*-Anisidine	Me	—$C_6H_4OMe(o)$	2-Amino-5-methylbenz-*o*-anisidide.	Aq. EtOH	98°	2.14	11 50	10.94
11.	Do	*p*-Anisidine	Me	—C_6H_4OMe (*p*)	2-Amino-5-methylbenz-*p*-anisidide.	EtOH	174°	1.60	10.90	10.94
12.	Do	2-Amino-4-(*p*-chloro-phenyl)-thiazole	Me		2-(2-Amino-5-methyl-benzamido)-4-(*p*-chloro-phenyl)-thiazole.	Glacial acetic acid	180°	1.20	12.10	12.19
13.	Do	2-Amino-4-phenyl-thiazole	Me		2-(2-Amino-5-methyl-benzamido)-4-phenyl-thiazole.	EtOH	175°	0.75	13.20	13.55

* From 2 g. of anhydride.

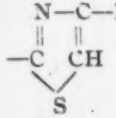
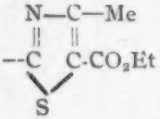
TABLE II

Sulphonamides of the structure



No.	Compound synthesised. Structure. R=	R₁=	Nomenclature.	Method used (A or B) & other conditions of reaction.	Cryst. from.	M.P.	* Yield.	% Nitrogen. Found	Calc.
1.	H	H	2-N⁴-Acetylsulphanilamidobenzamide.	A; left overnight and ether decanted off. Also B.	50% EtOH	255°	0.70 g.	12.80	12.61
2.	H	—Ph	2-N⁴-Acetylsulphanilamidobenzanilide.	A; left over 2 nights. Then refluxed for 3 hours and ether distilled off.	70% AcOH	188°	1.05	10.10	10.27
3.	H	*o*-tol.	2-N⁴-Acetylsulphanilamidobenz-*o*-toluidide.	B.	Gl. acetic acid	195°	0.40	10.00	9.94
4.	H	*m*-tol.	2-N⁴-Acetylsulphanilamidobenz-*m*-toluidide.	A; left overnight, refluxed for 3 hours and ether distilled off.	Do	165°	0.67	9.65	9.94
5.	H	*p*-tol.	2-N⁴-Acetylsulphanilamidobenz-*p*-toluidide.	A; slightly warmed, left overnight and ether decanted off.	Do	215°	1.18	9.87	9.94

TABLE II (*contd.*)

No.	Compound synthesised. Structure. R=	R$_1$=	Nomenclature.	Method used (A or B) & other conditions of reaction.	Cryst. from.	M. P.	*Yield.	% Nitrogen. Found.	Calc.
6.	H	—C_6H_4OMe (*p*)	2-N^4-Acetylsulphanilamidobenz-*p*-anisidide.	A; slightly warmed, left overnight and ether decanted off.	Gl. acetic acid.	200°	1.14	9.55	9.56
7.	H	—C_6H_4Cl (*p*)	2-N^4-Acetylsulphanilamidobenz-*p*-chloroanilde.	B; heated at 110-120°.	50% Acetic acid.	222°	0.74	9.50	9.47
8.	H		2-(2-N^4-Acetylsulphanilamidobenzamido)-4-phenylthiazole.	Do	Gl. acetic acid.	162°	0.36	11.70	11.48
9.	Me	—*m*-tol.	2-N^4-Acetylsulphanilamido-5-methylbenz-*m*-toluidide.	A; refluxed for 2 hours, ether distilled off & kept at 70-80° for another 30 minutes.	Do	228°	1 10	9 35	9.61
10.	Me	—*p*-tol	2-N^4-Acetylsulphanilamido-5-methylbenz-*p*-toluidide.	A; refluxed for 8 hours and ether distilled off.	Do	172°	0.87	9.45	9.61
11.	Me	—C_6H_4OMe (*p*)	2-N^4-Acetylsulphanilamido-5-methylbenz-*p*-anisidide.	Do	70% Acetic acid	222°	0.94	9.55	9.27
12.	Me		2-(2-N^4-Acetylsulphanilamido-5-methylbenzamido)-4-methyl-5-carbethoxythiazole.	B; heated at 115-120° for 1½ hrs.	Gl. acetic acid	195°	0.42	10.50	10.83

* From 1 g. of substituted amide.

† After keeping for a fortnight.

2-N^4-*Piperidinoacetylsulphanilamidobenzamide*.—The condensation between (VIII ; $R=R^1=H$; $X=Cl$) and piperidine was carried out as above. After distilling off the solvent, the residue was treated with 50 c. c. of water and neutralised with dilute acetic acid. The product was collected and crystallised from 50% ethanol in white needles, m.p. 184°, yield from 2 g. of (VIII) being 1.5 g. (Found : N, 13.20. $C_{20}H_{24}O_4N_4S$ requires N, 13.46 per cent).

2-N^4-*Morpholinoacetylaminosulphanilamidobenzamide* was prepared in the same manner as the above piperidino compound. The product crystallised from dilute ethanol in pale yellow needles, m.p. 188°, yield 0.76 g. from 1 g. of (VIII). (Found : N, 13.40. $C_{19}H_{22}O_5N_4S$ requires N, 13.39 per cent).

The authors are grateful to Dr. S. M. Mukherji for his kind interest in the work.

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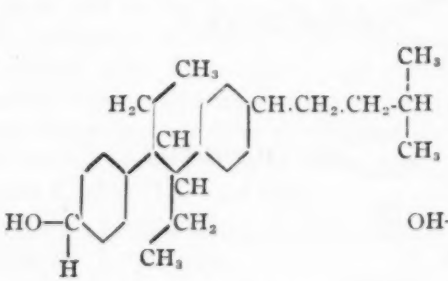
SYNTHESIS OF A COMPLETELY REDUCED ANALOGUE OF HEXESTROL. 1 : 2-DIETHYL-1-(4-METHOXY*cyclo*HEXYL)-2-(4-*iso*AMYL-*cyclo*HEXYL)-ETHANE

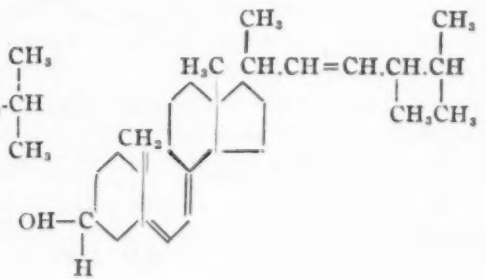
By (Miss) Sindhu Parkhi

1 : 2-Diethyl-1-(4-methoxy*cyclo*hexyl)-2-(4-*iso*amyl*cyclo*hexyl)-ethanol (III), obtained from 4-methoxyhexahydropropiophenone and the Grignard compound of ethyl-*p*-*iso*amylhexahydrobenzyl bromide, on dehydration with *p*-toluenesulphonic acid at 120° furnished the corresponding ethylene (IV) which on reduction with Adam's catalyst yielded the desired completely reduced product (V).

In a scheme to prepare antirachitic substances it was thought desirable to synthesise a completely reduced analogue of hexestrol with the modification of having a long alkyl chain at the end instead of a hydroxy group. This might possess antirachitic properties as its structural resemblance is apparent with calciferol. A corresponding relationship between hexestrol and estrone is well known.



[Reduced analogue of hexestrol]



[Calciferol]

The synthesis of the methyl ether of this compound has been achieved and is described herein.

The methyl ether of ethyl 4-hydroxy*cyclo*hexane carboxylate was prepared by the method of Owen and Robins (*J. Chem. Soc.*, 1949, 326); attempts to benzylate ethyl ester of the carboxylic acid resulted in a poor yield of the benzyl ether. The corresponding acid was obtained as an oil. The acid chloride of this acid was converted into 4-methoxyhexahydropropiophenone (I), using a cadmium Grignard reagent in 60% yield.

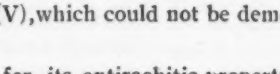
p-Hydroxy*iso*valerophenone (Close *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 1265) on the Clemmensen reduction afforded a 60% yield of *p*-*iso*amylphenol (Baranger, *Bull. soc. chim.*, 1931, *iv*, **49**, 1213). This was hydrogenated in a Parr bomb at 1500 lbs. pressure at 150° to furnish 4-*iso*amyl*cyclo*hexanol in 80% yield in the presence of Raney nickel. 4-*iso*Amyl*cyclo*hexanol was converted into the corresponding bromide, by boiling with hydrobromic-sulphuric acid mixture.

Propionitrile on treatment with the Grignard reagent, prepared from 4-*iso*amyl-*cyclo*hexyl bromide, afforded 4-*iso*amylhexahydropropiophenone (II).

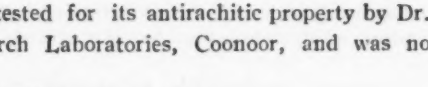
The compound (II) was reduced to 4-*iso*amylhexaydrophenylethyl carbinol in presence of Adam's catalyst at 60 lbs. pressure. This was converted into the bromide by phosphorus tribromide. The Grignard reagent of this bromide on reaction with 4-methoxyhexahydropropiophenone (I) afforded the tertiary alcohol (III), which was successfully dehydrated to (IV) by *p*-toluenesulphonic acid at 120°. The product was too small in quantity for separation into the isomeric forms. So it was directly hydrogenated with Adam's catalyst to (V), which could not be demethylated as the product was too small in quantity.

The compound was tested for its antirachitic property by Dr. V. N. Patwardhan, Director, Nutrition Research Laboratories, Coonoor, and was not found to possess any such property.

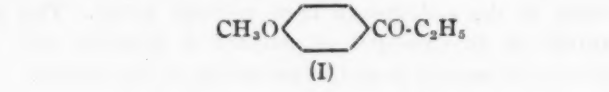
The following scheme indicates the method.



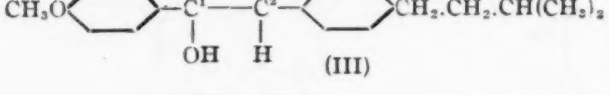
(I)



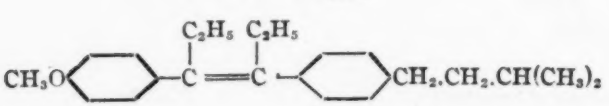
(II)



(III)



(IV)



(V)

EXPERIMENTAL

p-Hydroxybenzoic acid was prepared from salicylic acid by a modification of the method described in Organic Synthesis (Vol. 14, p. 48).

Dry potassium salicylate was suspended in liquid paraffin and heated in an oil-bath at 230°-240° for 3 hours. The product was poured into water and the aqueous layer separated; on acidification *p*-hydroxybenzoic acid was obtained as a slightly brown solid. This on crystallisation furnished the pure acid, m. p. 211-12°.

Ethyl *p*-hydroxy*cyclo*hexane carboxylate was prepared according to Owen and Robins (*loc. cit.*).

4-*Benzyloxy*cyclo*hexane Carboxylic Acid.*—Ethyl *p*-hydroxy*cyclo*hexane carboxylate (17 g.), pulverised sodium (2.3 g.) and dry benzene (50 c.c.) were refluxed till the sodium had reacted; benzyl chloride (15 g.) was then added and the mixture was refluxed for 16 hours with the addition of dry pyridine. The pyridine, benzyl chloride and benzene were removed by steam-distillation, and the residue was extracted with ether. This was hydrolysed by alcoholic KOH directly. On removing alcohol and acidification, 4-benzyloxy*cyclo*hexane carboxylic acid was obtained as a brown solid (8 g.). On crystallisation from ether, it melted at 109-110°. (Found: C, 71.5; H, 7.7; equiv., 235.4. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7 per cent. Equiv., 234).

The *amide*, prepared as usual, had m.p. 172-75°. (Found: N, 6.2. $C_{14}H_{19}O_2N$ requires N, 6.0 per cent).

4-*Benzyloxyhexahydropropiophenone.*—The above acid (5 g.) was refluxed with thionyl chloride (17 g.) for 3 hours. Excess of the latter was removed under reduced pressure and the residue was dissolved in dry benzene (20 c.c.). This was added to a cadmium Grignard [prepared from ethyl bromide (20 g.), magnesium (4 g.), cadmium chloride (9 g) and ether (20 c.c.)] in an atmosphere of nitrogen in three lots at 0° with stirring in course of 1 hour; the mixture was allowed to reach the room temperature at which it was stirred for a further period of 3 hours It was decomposed with dilute H_2SO_4 and water, and extracted with benzene. After washing, drying and removal of the solvent it afforded a residue which could be distilled under reduced pressure (2mm.) yielding a semi-solid substance which was crystallised from methyl alcohol (2 g.), m.p. 55-58°. (Found: C, 77.9; H, 9.1. $C_{16}H_{22}O_2$ requires C, 78.2; H, 9.0 per cent).

The 2:4-*dinitrophenylhydrazone* melted at 121-22°. (Found: N, 13.3. $C_{22}H_{26}O_5N_4$ requires N, 13.1 per cent).

4-*Methoxy*cyclo*hexane Carboxylic Acid.*—Ethyl 4-methoxy*cyclo*hexane carboxylate was prepared according to Owen and Robins (*loc. cit.*). The above ester was hydrolysed to the acid, b.p. 150°-165°/25 mm. The long boiling point range showed that the ester consisted of stereoisomers. As the quantity was small the isomers could not be separated. (Found: C, 60.6; H, 8.8. $C_8H_{14}O_3$ requires C, 60.8; H, 8.8 per cent).

4-*Methoxyhexahydropropiophenone* (I).—The above acid (10 g.) and thionyl chloride (35 g.) were refluxed for 3 hours till the evolution of hydrogen chloride had ceased. After removing the excess of thionyl chloride, the residue was distilled under reduced pressure, b.p. 120°-140°/20 mm., yield 8 g.

To a cold solution of diethylcadmium in benzene [prepared from ethyl bromide (28 g.), magnesium (6 g.), cadmium chloride (14 g.), and ether (100 c.c.)], a benzene solution of the acid chloride from 4-methoxy*cyclo*hexane carboxylic acid (8 g.) was added in an atmosphere of nitrogen. The mixture was kept overnight and then stirred for 3 hours at 25°-35°. It was decomposed by ice and dilute H_2SO_4 and extracted with benzene. The benzene extract on drying and removal of the solvent was

distilled under reduced pressure, b.p. 220°-240°/15 mm., yield 3.5 g. *d*, 0.9772; n_D^{25}, 1.468; $(MR)_D$, 48.4 (calc. 48.3). (Found: C, 70.5; H, 10.8. $C_{16}H_{18}O_2$ requires C, 70.7; H, 10.6 per cent).

Its *semicarbazone*, prepared as usual, had m.p. 174-75°. (Found: N, 17.9. $C_{11}H_{21}O_2N_3$ requires N, 17.7 per cent).

4-iso*Amyl*cyclo*hexanol*.—*p*-Hydroxy*iso*valerophenone, prepared according to Close *et al.* (*loc. cit.*), was reduced to *p-iso*amylphenol by the Clemmensen reduction according to Baranger (*loc. cit.*), b.p. 121°/14 mm. *p*-isoAmylphenol was catalytically reduced to *p-iso*amyl*cyclo*hexanol in a Parr bomb (Ungnadd and Melaren, *J. Amer. Chem. Soc.*, 1944, **66**, 118), in the presence of Raney nickel as a catalyst at 1500 lbs. pressure at 150°, b.p. 155°-165°/5 mm. (Found: C, 77.4; H, 13.1. $C_{11}H_{22}O$ requires C, 77.7; H, 12.9 per cent).

p-iso*Amyl*cyclo*hexyl bromide* was prepared from *p-iso*amyl*cyclo*hexanol (50 g.) and HBr-H_2SO_4 mixture (175 c.c.) according to the method given in "Organic Synthesis" (Vol. 19, p. 88), (20 g.), b.p. 162°-167°/20 mm. (Found: Br, 34.4. $C_{11}H_{21}Br$ requires Br, 34.3 per cent).

4-iso*Amylhexahydropropiophenone* (II).—A Grignard reagent was prepared from *p-iso*amyl*cyclo*hexyl bromide (34 g.) magnesium (3.5 g.), and ether (150 c.c.). To this solution propionitrile (8 g.) was added with stirring at 0°. The mixture was kept overnight, decomposed by ice and ammonium chloride, and extracted with ether. The ether extract on drying and removal of the solvent afforded a residue which was distilled under reduced pressure, (20 g.), b.p. 130°-135°/5 mm. *d*, 0.9979; n_D^{25}, 1.94; $(MR)_D$, 64.9 (calc. 65.1). (Found: C, 79.7; H, 12.5. $C_{14}H_{26}O$ requires C, 80.0; H, 12.4 per cent).

Its *semicarbazone*, prepared as usual, had m.p. 193-94°. (Found: N, 15.5. $C_{15}H_{29}ON_3$ requires N, 15.7 per cent).

4-iso*Amylhexahydrophenylethyl Carbinol*.—The compound (II, 19 g.) was hydrogenated over platinum oxide (4 g.) as a catalyst for 10 hours at 60 lbs. pressure. The carbinol formed had b.p. 150°-164°/25 mm., yield 10 g. (Found: C, 79.0; H, 13.1. $C_{14}H_{28}O$ requires C, 79.3; H, 13.7 per cent).

Ethyl-p-iso*amylhexahydrobenzyl Bomide*.—The preceding compound (10 g.), PBr_3 (7 g.) and benzene (25 c.c.) were mixed and kept overnight, and on the next day refluxed for 2 hours. The contents were poured into ice-water, and extracted with ether. The ether extract after drying and removing the solvent was distilled under reduced pressure, b.p. 120°-150°/35 mm., yield 5.5 g. (Found: Br, 28.1. $C_{14}H_{27}Br$ requires Br, 28.6 per cent).

1 : 2-*Diethyl*-1-(4-*methoxy*cyclo*hexyl*) - 2 - (4-iso*amyl*cyclo*hexyl*)-*ethylene* (IV).—The compound (I, 3 g.) was added to the Grignard reagent {prepared from the above (5 g.), magnesium (0.5 g.) and ether (50 c.c.)}, cooled to 0°. It was kept overnight and refluxed for 2 hours. The product was decomposed by ice-sulphuric acid, and extracted with ether. The ether extract, after drying and removing the solvent, furnished an oily product (3.5 g.), 1:2-diethyl-1-(4-methoxy*cyclo*hexyl)-2-(4-*iso*amyl-*cyclo*hexyl)-ethanol (III).

The above product (3.5 g.) was dehydrated by heating the mixture in an oil-bath at 120°-125° with *p*-toluenesulphonic acid (1 g.) for 3 hours. The contents were then poured into water, extracted with ether, washed with sodium carbonate solution, followed by water. The ether extract after drying and removing the solvent was distilled under reduced pressure, b.p. 185°-190°/3 mm., (2 g.), affording a mixture of red oil and a yellow solid which sublimed at the beginning of the distillation. The solid was in all probability an isomer but was small in quantity for isolation. (Found : C, 82.5 ; H, 12.5. $C_{24}H_{44}O$ requires C, 82.8 ; H, 12.6 per cent).

1:2-*Diethyl*-1-(4-*methoxy*cyclo*hexyl*)-2-(4-iso*amyl*cyclo*hexyl*)-*ethane* (V).—The above compound (IV, 2 g.) was then reduced to 1 : 2-diethyl-1-(4-methoxy*cyclo*hexyl)-2-(4-*iso*-amyl*cyclo*hexyl)-ethane by platinum oxide as a catalyst (0.5 g.) at 60 lbs. pressure and had b.p. 195°/3 mm., yield 1.4 g. (Found : C, 82.1 ; H, 13.2. $C_{24}H_{46}O$ requires C, 82.3 ; H, 13.1 per cent).

The author takes this opportunity to express her grateful thanks to Principal B.V. Bhide, S.P. College, Poona, who suggested this problem, for helpful guidance and encouragement throughout the pro ress of this work. Thanks are also due to Dr. M. Damodaran, Director, Biochemistry Section, National Chemical Laboratory, Poona, for allowing the use of the high pressure hydrogenation equipment.

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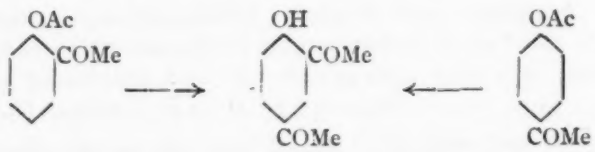
STUDIES IN FRIES MIGRATION. PART XIV. THE FRIES ISOMERISATION OF ACYL ESTERS OF *o*- AND *p*-HYDROXY-ACETOPHENONES AND *p*-HYDROXYBENZOPHENONE

By M. R. Bhatt and N. M. Shah

Fries isomerisation of acyl esters of *o*- and *p*-hydroxy-acetophenones to 2-hydroxy-5-acetylacetophenone and acyl and benzoyl esters of 2-hydroxybenzophenone to 3-acetyl- and 3-benzoyl-4-hydroxybenzophenone respectively has been effected.

The Fries migration of a number of negatively substituted phenolic esters has been investigated in recent years (Brown, *J. Amer. Chem. Soc*, 1946, **68**, 873; Shah and Shah, this *Journal*, 1949, **26**, 237; Amin and Shah, *ibid.*, 1952, **29**, 351, 915; *Curr. Sci.*, 1952, **21**, 246; Chaughuley and Amin, *Science & Culture*, 1954, **19**, 614), but the information regarding the migration of acyl esters of hydroxyacetophenones and benzophenones appears to be scanty (Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56). In the present investigation therefore, the Fries isomerisation of *o*- and *p*-acetoxy-acetophenones and *p*-acyloxybenzophenone has been investigated. Treatment of *o*-acetoxy-acetophenone with anhydrous aluminium chloride at temperatures ranging from 120° to 170° yielded only a pasty mass, but on carrying out this reaction in nitrobenzene as a solvent at room temperature, a diketone of m.p. 93-94° was obtained. *p*-Acetoxy-acetophenone on similar treatment furnished only the deacetylated product, but on heating this compound with anhydrous aluminium chloride at 140°-150° in absence of a solvent, the diketone of m.p. 93-94°, identical with the previous one, was obtained. This diketone has been assigned the constitution, 2-hydroxy-5-acetylacetophenone as:



(*i*) In the first case the migration took place at room temperature. It is more likely that the acetyl group has migrated to *para* position with respect to OH group. (*ii*) In the case of *p*-acetoxyacetophenone, the migration can only take place in the *ortho* position, the *para* position being occupied. This diketone responds to Pyman's test, showing the presence of ketonic group in the *ortho* position. (*iii*) Both the diketones on methylation and subsequent oxidation by alkaline permanganate yield 1-methoxy-*iso*phthalic acid, m.p. 261° (Schall, *Ber.*, 1879, **12**, 828; Stoermer and Behn, *Ber.*, 1901, **34**, 2458).

The migration of acetyl and benzoyl esters of *p*-hydroxybenzophenone was similarly carried out at 160°-165° without a solvent, 3-acetyl- and 3-benzoyl-4-hydroxybenzophenone respectively being obtained.

EXPERIMENTAL

Fries Migration of o- *and* p-*Acetoxyacetophenones*: *Formation of* 2-*Hydroxy*-5-*acetylacetophenone*.—(*i*). *o*-Acetoxyacetophenone, prepared by acetic anhydride-pyridine method, crystallised from alcohol in white needles, m.p. 88-89°. Friedländer and Neudorfer (*Ber.*, 1897, **30**, 1080) report the same melting point.

To aluminium chloride (7.5 g., 3.3 *M*), dissolved in dry nitrobenzene (30 c.c.), *o*-acetoxyacetophenone (3 g., 1 *M*.) was added gradually with stirring and cooling under tap. It was left overnight at room temperature ($CaCl_2$ guard-tube) and then treated with crushed ice and HCl (conc., 3 c.c.) and steam-distilled. The hot residual liquid was filtered off to remove some tarry matter; the filtrate on cooling deposited white lustrous needles, which were collected and crystallised from dilute alcohol, m.p. 92-93°, yield 1.3 g. (Found: C, 67.3; H, 5.4. $C_{10}H_{10}O_3$ requires C, 67.4; H, 5.6 per cent).

(*ii*). *p*-Acetoxyacetophenone, prepared as before, crystallised from hot water containing a little alcohol in flat needles, m.p. 54-55°. Verley (*Bull. soc. chim.*, 1898, *iii*, **19**, 140) reports m.p. 54°.

An intimate mixture of *p*-acetoxyacetophenone (3 g., 1.1 *M*.) and anhydrous aluminium chloride (7.5 g., 3.3 *M*.) was heated at 140°-150° for an hour ($CaCl_2$ guard-tube) when HCl fumes copiously evolved. On decomposing the cold reaction mixture with ice and HCl (conc.), a solid separated which was crystallised from dilute acetic acid in needles, m.p. 92-93°, yield 1.2 g. (mixed m.p. with the migration product of *o*-acetoxyacetophenone being undepressed).

The 2:4-*dinitrophenylhydrazone* crystallised from dilute alcohol in reddish needles, m. p. 189-90°. (Found: N, 20.65. $C_{22}H_{17}O_9N_8$ requires N, 20.85 per cent).

The *methyl ether*, prepared by dimethyl sulphate-potassium carbonate-acetone method, crystallised from dilute alcohol in pale yellow needles, m.p. 86°. (Found: C, 68.55; H, 6.40. $C_{11}H_{12}O_3$ requires 68.75; H, 6.25 per cent).

Fries Migration of p-*Acetoxybenzophenone*: *Formation of* 3-*Acetyl*-4-*hydroxybenzophenone*.—*p*-Acetoxybenzophenone, prepared by acetic anhydride-pyridine method, crystallised from alcohol in white needles, m.p. 81-82°. Döbner and Stackmann (*Ber.*, 1877, **10**, 1970) report the same melting point.

An intimate mixture of *p*-acetoxybenzophenone (3 g., 1 *M*.) and anhydrous aluminium chloride (5.5 g., 3.3 *M*) was heated at 150°-160° for about an hour ($CaCl_2$ guard-tube). On working it up, the product crystallised from dilute acetic acid in rhombic prisms, m.p. 102-103°. (Found: C, 75.5; H, 4.9. $C_{15}H_{12}O_3$ requires C, 75.0; H, 5.0 per cent). It develops a violet colour with alcoholic ferric chloride and dissolves in alkali with a yellow colour.

The *semicarbazone*, prepared as usual, crystallised from dilute alcohol in yellow needles, m.p. 249-50° (decomp.). (Found N, 23.6. $C_{17}H_{17}O_3N_6$ requires N, 23.8 per cent).

The *methoxy derivative*, prepared by dimethyl sulphate-alkali method, crystallised from alcohol in tiny flat needles, m.p. 108-109°. (Found: C, 75.5. H, 5.4. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5 per cent).

Fries Migration of p-*Benzoyloxybenzophenone* : *Formation of* 3-*Benzoyl*-4-*hydroxybenzophenone*.—The *p*-benzoyloxybenzophenone, prepared by benzoyl chloride-pyridine method, crystallised from alcohol in lustrous needles, m.p. 112°.

p-Benzoyloxybenzophenone (3 g.) and anhydrous aluminium chloride (4·5 g., 3·3 *M*) were intimately mixed and heated at 160°-165° for an hour ($CaCl_2$ guard-tube). On working up the product as before, the substance obtained was crystallised from dilute alcohol in tiny needles, m.p. 105-106°. Pieroni (*Gazzetta*, 1932, **62**, 387) reports the same m.p.

The *benzoyloxy derivative*, prepared as before, crystallised from benzene in needles, m.p. 144-45°. (Found : C, 83.0 ; H, 4.0. $C_{27}H_{18}O_4$ requires C, 83.2 ; H, 3.7 per cent).

The *oxime*, prepared as usual, crystallised from alcohol in colorless needles, m.p. 214° (decomp.). (Found : N, 13.0. $C_{20}H_{16}O_3N_2$ requires N, 13.2 per cent).

Thanks are due to Shri A. A. Raval, M.Sc. for his help in experimental work.

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SETTING OF THE GELS OF SODIUM OLEATE AND STEARATE IN SOME ORGANIC SOLVENTS. PART I. TIME AND TEMPERATURE OF SETTING

By K. B. Deshpande and K. P. Buch

The study of the time and temperature of setting of gels of sodium oleate in nujol, pinene and xylene and of sodium stearate in nujol and benzyl alcohol has shown that (1) the time of setting for any concentration depends upon the rate of cooling; (2) the setting temperature of a given system is constant and independent of the rate of cooling, but increases with increase in concentration of the soap in the system.

Most of the organic gels are formed either by cooling or by heating the gel-forming systems. Hence, the time of setting of organic gels should necessarily be determined by factors which influence the rate of cooling of the gel-forming solutions. This fact was realised by Trotman and Ball and others (*J. Soc. Chem. Ind.*, 1934, **53**, 225T; *Curr. Sci.*, 1940, **9**, 119, 459) who took the time of setting of an organic gel to be "the time required by a solution prepared at a high temperature to set when cooled in a thermostat maintained at a constant low temperature". Their results bring out clearly that the time of setting of an organic gel increases with the increase in the temperature of the surrounding.

The previous work has laid stress on the time of setting of gels as a fundamental property of the system. The importance of the temperature of setting does not seem to have received corresponding notice. In the present investigation the effects of concentration and the rate of cooling on the time and temperature of setting have been studied systematically in the case of the gel-forming solutions of sodium oleate in nujol, xylene and pinene and of sodium stearate in nujol and benzyl alcohol.

Experimental

Sodium oleate and stearate were products of B.D.H. Nujol (d 0.8743; μ 1.4810) was obtained from Messers. Stanco Incorporated, New Jersey, U S.A. Benzyl alcohol was a superfine product of W. J. Bush and Co.. The purity of pinene and xylene was checked by determining their boiling points from time to time.

Gel-forming Solutions.—Gels of sodium oleate in nujol, pinene and xylene were prepared in the usual manner (Prasad and Hattiangdi, *Proc. Ind. Acad. Sci.*, 1945, **21A**, 1) in boiling tubes of internal diameter 2.8 cm.. The soap initially swelled and finally went into solution at 200°, 140° and 130° respectively. Gels of sodium stearate in nujol and benzyl alcohol were prepared similarly in boiling tubes of the same diameter. The soap initially swelled and finally went into solution at 200° and 110° respectively.

Time and Temperature of Setting.—The time of setting was determined by the Flemming's method (*Z. physikal. Chem.*, 1902, **41**, 427). The effect of rate of cooling

on the time of setting was determined in two ways, namely, by keeping the solutions prepared at temperatures mentioned (*i*) at several lower temperatures and (*ii*) at each such temperature in tubes of internal diameters 2.2 and 3.2 cm. as well.

The temperature of setting was determined as follows: A thermometer was inserted at the centre of the tube containing the solution after all the air bubbles were removed. The tube was then transferred to a thermostat maintained at some constant low temperature. The gel-forming solution was periodically examined to determine whether it had set to a gel. The temperature indicated at the point of setting was taken to be the temperature of setting. The exact temperature of setting was determined by repeating the experiment several times.

DISCUSSION

The general nature of results is the same in all cases. They lead to the following conclusions:

(*i*) The time of setting for any concentration depends on the rate of cooling; it inereases as the rate of cooling is reduced and *vice versa*.

(*ii*) Under identical conditions of cooling, the solutions of higher soap content take shorter time to set.

(*iii*) For a given concentration, the setting temperature is constant and is independent of the rate of cooling.

(*iv*) The setting temperature increases as the concentration of the soap is increased.

It was also noted independently that when a solution was kept in a thermostat maintained at a temperature even one degree higher than the setting temperature of the solution, it did not set to a rigid gel but afforded a highly viscous mass. These observations establish that the setting temperature is the highest temperature at which a gel-forming solution sets to a gel and that all the processes are involved in the setting of a gel during the cooling of the solution from T_s, the temperature at which it has been prepared, to T_g, the temperature of setting.

It appears from the above that the time of setting of these gels is the time taken by the gel-forming solutions from T_s to T_g, when cooled in a thermostat kept at a given temperature T_o. This conclusion was verified by the study of the cooling curves of the gel-forming solutions under the same conditions as employed for the determination of the time of setting. It was found that the cooling of the solutions obeyed the Newton's law before, during and after gelation; the values of the time (T_c) required for cooling of a solution from T_s to T_g, when cooled at T_o, calculated by applying the equation

$$\log (T_s - T_o) - \log (T_g - T_o) = Kt_c,$$

agreed fairly well with the corresponding observed values for the time of setting.

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INTERACTION OF THIONYL CHLORIDE AND AROMATIC HYDROXY KETONES IN PRESENCE OF FINELY DIVIDED COPPER. PART VIII. PREPARATION OF 3:3′-DIBUTYRYL-4:6-4′:6′-TETRAHYDROXY-DIPHENYL THIOETHER AND ITS DERIVATIVES FROM RESBUTYROPHENONE

By V. J. Dalvi and G. V. Jadhav

Preparation of 3:3′-dibutyryl-4:6-4′:6-tetrahydroxydiphenyl thioether and its tetra-acetoxy, dimethoxy and tetramethoxy derivatives is described. Nitration and bromination as well as 2:4-dinitrophenylhydrazone derivative of the tetrahydr xy thioether are also described.

Present work is the continuation of the work under publication. The reaction was carried out in presence of dry chloroform at room temperature, affording the thioether (I). Its constitution was arrived at by the formation of a nitroresbutyrophenone by the action of nitric acid on it below 10°. It is found to be different from authentic 3-nitroresbutyrophenone (2:4-dihydroxy-3-nitrobutyrophenone), prepared from 2-nitroresorcinol by Friedel and Crafts' reaction, and therefore it is given the constitution 2:4-dihydroxy-5-nitrobutyrophenone. This constitution has further been confirmed by its identity with the nitration product of resbutyrophenone. This shows that the two nuclei are linked through sulphur atoms in the position *para* to -OH group and *meta* to $-COC_3H_7$ group, and hence, the thioether is 3:3′-dibutyryl-4:6-4′:6′-tetrahydroxydiphenyl thioether (I).

Bromination of the thioether (I) with bromine, slightly more than two molecules for one of (I) in acetic acid, furnishes the dibromo-thioether (V), which constitution is supported by the formation of 2:4-dihydroxy-3-bromo-5-nitrobutyrophenone (VI) by the action of nitric acid on it, as proved by its mixed melting point with a genuine specimen prepared by bromination of 2:4-dihydroxy-5-nitrobutyrophenone in acetic acid medium.

With excess of liquid bromine, 2:4:6-tribromoresorcinol is obtained, showing that bromine oxidises the ketonic group to -COOH group which loses carbon dioxide, and the resulting resorcinol is brominated. Tetra-acetoxy (II), dimethoxy (III) and tetramethoxy (IV) derivatives and 2:4-dinitrophenylhydrazone of (I) have been prepared. The thioether (III) is also obtained from 4-methoxy-2-hydroxybutyrophenone by the action of thionyl chloride in presence of copper as well as by the action of sulphur monochloride and of sulphur dichloride.

Thioether (I) is also obtained from resbutyrophenone by the action of sulphur monochloride as well as f sulphur dichloride in ethereal solution.

Experimental

3:3′-Dibutyryl-4:6--4′:6′-tetrahydroxydiphenyl Thioether (I).—Thionyl chloride (12 c.c.) was added to the ice-cooled solution of resbutyrophenone (14.5 g.) in dry

chlorofrom (80 c.c.). Copper powder (8 g.) was then added in small lots (over 1 hour). The reaction mixture was left overnight at room temperature and then filtered and the residue washed with chloroform. A dark brown semi-solid remained after removal of the chloroform (room temperature). It was first washed with petroleum ether (b.p. 40°-60°) and then treated with benzene when it solidified. It was finally crystallised from dilute alcohol in colorless needles, m.p. 170-71°, yield 5 g. (Found : C, 61.6; H, 6.0; S, 8.2. $C_{20}H_{22}O_6S$ requires C, 61.5; H, 5.6; S, 8.2 per cent).

It is easily soluble in alcohol, acetone and chloroform and sparingly so in benzene, and insoluble in petroleum ether. It develops a red coloration with alcoholic ferric chloride and is soluble in dilute alkali with a yellow colour.

The same thioether was also formed when resbutyrophenone (3.6 g.), dissolved in dry ether (50 c.c.) and cooled in ice, was treated with (*i*) sulphur monochloride (1 c.c.) or (*ii*) sulphur dichloride (1.5 c.c.), and the reaction was allowed to proceed for 1 hour at room temperature in the first case, and for ½ hour in the second case.

In the first case the pasty mass, obtained after removal of the ether, was first shaken with petroleum ether and then extracted with alcohol. The solid obtained after removal of alcohol was washed with benzene and then crystallised from dilute alcohol in needles, m.p. 170-71°, yield 0.5 g.

In the second case the pasty mass, obtained after removal of the ether, was boiled with water and then first crystallised from acetic acid and finally from dilute alcohol, m.p. 170-71°, yield 0.5 g.

Tetra-acetoxy Derivative of (I) [II] was prepared by acetylating (I) with acetic anhydride in presence of pyridine. It was first crystallised from dilute alcohol and finally from petroleum ether, m.p. 98-99°. (Found : S, 5.6. $C_{28}H_{30}O_{10}S$ requires S, 5.7 per cent).

3 : 3′-Dibutyryl-4 : 4′-dihydroxy-6 : 6′-dimethoxydiphenyl thioether (III) was obtained by methylating (I, 0.5 g.) with dimethyl sulphate (0.3 c.c.) in dry acetone medium (20 c.c.) in presence of anhydrous potassium carbonate (1 g.) by refluxing the mixture on a water-bath for 10 hours. The solid obtained from acetone was crystallised from alcohol in white needles, m.p. 155-56°. (Found : S, 7.6. $C_{22}H_{26}O_6S$ requires S, 7.7 per cent). It shows a bluish green coloration with alcoholic ferric chloride and is soluble in dilute alkali with a yellow colour.

The same substance was also obtained when copper powder (2 g.) was gradually added (over 1 hour) to a cooled solution of 2-hydroxy-4-methoxybutyrophenone (4 g.) in dry chloroform (20 c.c.) and thionyl chloride (3 c.c.). Chloroform was filtered next day and the pasty mass, left after removal of the chloroform (at room temperature), was first washed with petroleum ether and then boiled with water. The semi-solid mass was first crystallised from acetic acid and then from dilute alcohol in colorless needles, m.p. 155-56°.

It was also obtained by the action of (*i*) sulphur monochloride (1 c.c.) or (*ii*) sulphur dichloride (1.5 c.c.) on ice-cooled dry ethereal solution of 2-hydroxy-4-methoxybutyrophenone (4 g. in 50 c.c.) and working up in the same way as in the case of thionyl chloride reaction.

Tetramethoxy derivative of (I) [IV] was prepared by methylating (I) with excess of dimethyl sulphate in acetone medium in presence of 4% KOH solution by heating it in a water-bath for 1 hour. The white solid separating was crystallised from alcohol in needles, m.p. 165-66°. (Found : S, 7.0. $C_{24}H_{30}O_6S$ requires S, 7.2 per cent).

2 : 4-*Dinitrophenylhydrazone* of the thioether (I) was obtained as red plates from acetic acid, m.p. 255-56° (decomp.). (Found : N, 14.9. $C_{32}H_{30}O_{12}N_8S$ requires N, 14.9 per cent).

2 : 4-*Dihydroxy-5-nitrobutyrophenone*.—The thioether (I, 1 g.) was gradually added to ice-cooled nitric acid (*d* 1.4, 10 c.c.). The reaction was allowed to proceed at that temperature for about 2 hours and then diluted with ice. The solid obtained was crystallised from dilute alcohol in shining yellow needles, m.p. 120-21°. (Found : N, 6.4. $C_{10}H_{11}O_5N$ requires N, 6.2 per cent) (mixed m.p. with the authentic specimen prepared by the action of nitric acid in presence of acetic acid on 2 : 4-dihydroxybutyrophenone).

3 : 3′-*Dibutyryl*-4 : 6-4′ : 6′-*tetrahydroxy* - 5 : 5′ - *dibromodiphenyl Thioether* (V).—A solution of bromine in acetic acid (32 c.c. of 10% solution, w/v) was added to the hot solution of the thioether (I, 3.5 g.) in acetic acid (20 c.c.). A white bromo derivative soon separated which was crystallised from acetic acid in colorless needles, m.p. 216-17°, yield 2.5 g. (Found : Br, 29.0. $C_{20}H_{20}O_6Br_2S$ requires Br, 29.2 per cent).

2 : 4 : 6-*Tribromoresorcinol*.—Liquid bromine (5 c.c.) was added to the thioether (1 g.) when it went into solution. The reaction was allowed to proceed overnight. The liquid was then diluted and the solid separating was washed with sodium bisulphite and crystallised from hot water, m.p. 110-11°. No lowering in melting point was observed when mixed with a genuine specimen prepared from resorcinol according to Benedikt (*Monatsh.*, 1883, **4**, 227).

2 : 4-*Dihydroxy-3-bromo-5-nitrobutyrophenone* (VI).—The thioether (V, 1 g.) was suspended in acetic acid (10 c.c.), and nitric acid (*d* 1.4, 5 c.c.) was added to it and warmed on a boiling water-bath until a clear solution was formed. It was then poured over ice and the solid obtained was crystallised from dilute alcohol in pale yellow needles, m.p. 120-21°. (Found : Br, 26.2. $C_{10}H_{10}O_5NBr$ requires Br, 26.3 per cent).

It showed no lowering in melting point with the genuine specimen prepared by brominating 5-nitroresbutyrophenone in acetic acid medium.

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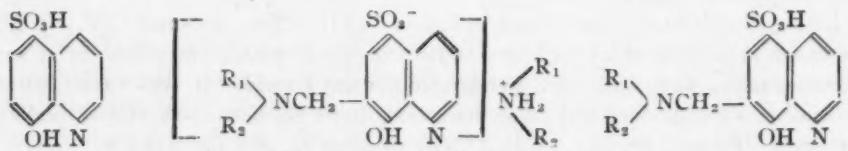
POSSIBLE ANTIAMOEBIC AGENTS. MANNICH BASES FROM 8-HYDROXYQUINOLINES

By A. B. Sen and Yashwant D. Kulkarni

Several Mannich bases have been prepared from 8-hydroxyquinoline-5-sulphonic acid, with a view to testing their antiamoebic activity.

Substituted 8-hydroxyquinolines, viz., di-iodoquin, vioform and chiniofon, are important amoebacidal drugs. Burckhalter and Edgerton (*J. Amer. Chem. Soc.*, 1951, **73**, 4837), Edgerton and Burckhalter (*ibid.*, 1952, **74**, 5209) and Burckhalter *et al.* (*ibid.*, 1954, **76**, 4902) have observed interesting amoebacidal activity in a group of compounds obtained by substituting dialkylaminoalkyl groupings by the Mannich reaction for the iodine atom in vioform. This prompted the authors to make a similar replacement of the iodine atom in chiniofon by dialkylaminoalkyl groupings and to study the antiamoebic activity of the resulting compounds (III).

The Mannich reaction with hydroxyquinolines has not been extensively studied ; a few reactions of 8-hydroxyquinoline with dimethylamine, morpholine, piperidine and formaldehyde are described in the literature (Ger. Pat. 92309 ; Frdl., 1899, **4**, 103) and that 4-hydroxyquinolines have been submitted to the Mannich reaction by Price and Jackson (*J. Amer. Chem. Soc.*, 1946, **68**, 1282). The present work was therefore undertaken to study this reaction in greater details with 8-hydroxyquinoline 5-sulphonic acid (I).



(I) (II) (III)

8-Hydroxyquinoline-5-sulphonic acid (I), required for the work, was obtained by the method of Matsumara (*ibid.*, 1927, **49**, 810). For the preparation of the Mannich bases the sodium salt of compound (I), different secondary amines and formaldehyde were employed, adopting the same procedure described earlier (Ger. Pat., 92309; Frdl., *loc. cit.*). It was, however, observed that only in the case of piperidine, the Mannich base could be separated successfully from the starting material, but with other secondary amines the expected Mannich bases could not be isolated in the pure form.

The Mannich reaction with the free sulphonic acid (I) instead of its sodium salt was also carried out, and it was found that the amine salts (II) of the expected Mannich bases (III) were produced. The lower secondary amines, viz., dimethylamine, diethylamine, di-*n*-propylamine and diethanolamine, however, did not furnish the amine salts, but yielded the Mannich bases directly. This may be ascribed to the instability of the

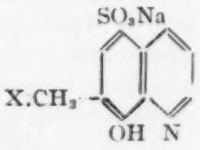
lower amine salts. The isolation of the free Mannich bases from their amine salts was achieved by acidifying the hot alcoholic solution of the salts with acetic acid and cooling the mixture.

EXPERIMENTAL

8-Hydroxyquinoline-5-sulphonic Acid (I) *and its Sodium Salt.*—(I) was prepared according to the method of Matsumara (*loc. cit.*). From 14½ g. of 8-hydroxyquinoline only 20 g. of the sulphonated product (I), m.p. 310°, could be obtained, yield 80% (reported 96%[1]). The sodium salt was prepared by suspending the sulphonic acid in hot water and neutralising with sodium carbonate. On cooling, the sodium salt crystallised out.

Sodium Salt of 7-sec.-Aminomethyl-8-hydroxyquinoline-5-sulphonic Acid.—A mixture of the sodium salt (2.47 g., 0.01*M*), paraformaldehyde (0.3 g., 0.01*M*) and the secondary amine (0.1*M*) in 150 c.c. of alcohol was refluxed for 6 hours on a water-bath. The mixture was then concentrated under reduced pressure and the yellow solid obtained was washed with alcohol and finally crystallised from *n*-butanol-ether mixture (1 : 5). The m. p., yields and % sulphur of the compounds are recorded in Table I.

TABLE I



No	X=	M. P.	Yield.	Mol. formula.	% Sulphur. Found.	Calc.
1	Piperidino-	281°	75%	$C_{15}H_{17}O_4N_2SNa$	8.90	9.30
2	Morpholino-	284°	80	$C_{14}H_{15}O_5N_2SNa$	10.32	0.25
3	Diethylamino-	286°	85	$C_{14}H_{17}O_4N_2SNa$	10.64	9.64

sec.-Amine Salts of 7-sec.-Aminomethyl-8-hydroxyquinoline-5-sulphonic Acid.—A mixture of 8-hydroxyquinoline-5-sulphonic acid (I) (2.25 g., 0.01*M*), paraformaldehyde (0.3 g., 0.01*M*) and 0.1*M* in the above case of piperidine and morpholine and 0.05*M* with di-*n*-butylamine and di-*iso*butylamine, in 30-50 c.c. alcohol, was heated under reflux over a water-bath for 6 hours. The mixture was then concentrated under reduced pressure and the residue washed with ether. The, solid, thus obtained, was crystallised from acetone-alcohol mixture (1 : 1). The m. p., yield and % sulphur of the compounds obtained are shown in Table II.

TABLE II

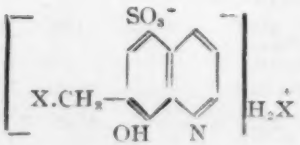
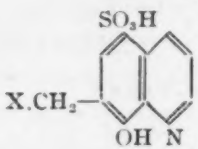


TABLE II (*contd.*)

No.	X=	M. P.	Yield.	Mol. formula.	%Sulphur. Found.	Calc.
1	Di-*n*-butylamino-	182-83°	50%	$C_{26}H_{45}O_4N_3S$	6.34	6.46
2	Di-*iso*butylamino-	151-52°	60	$C_{26}H_{45}O_4N_3S$	6.21	6.46
3	Piperidino-	194-95°	80	$C_{20}H_{23}O_4N_3S$	7.90	7.86
4	Morpholino-	184-85°	85	$C_{18}H_{25}O_6N_3S$	7.75	7.79

The isolation of the free sulphonic acids from the above amine salts was achieved by acidifying the hot alcoholic solution of the salts (1 g. of the salt in 10 c.c. of alcohol) with acetic acid and cooling the mixture. The crystals which separated out were filtered and washed with boiling alcohol. Their m.p., yields (based on their conversion from the amine salts) and their analysis (% sulphur) are recorded in Table III (compounds 5-8).

TABLE III



No.	X=	M. P.	Yield.	Mol. formula.	% Sulphur. Found.	Calc.
1	Dimethylamino-	198-200°	71%	$C_{21}H_{14}O_4N_2S$	11.12	11.35
2	Diethylamino-	223-24°	66	$C_{14}H_{18}O_4N_2S$	10 23	10 32
3	Di-*n*-propylamino-	166-67°	65	$C_{16}H_{22}O_4N_2S$	9.13	9.47
4	Di-ethanolamino-	177-78°	60	$C_{14}H_{18}O_6N_2S$	9.15	9 35
5	Di-*n*-butylamino-	206-208°	75	$C_{18}H_{26}O_4N_2S$	8 61	8 74
6	Di-*iso*butylamino-	199 200°	70	$C_{16}H_{26}O_4N_2S$	8.62	8.74
7	Piperidino-	211°	80	$C_{15}H_{18}O_4N_2S$	9 81	9 93
8	Morpholino-	213-14°	85	$C_{14}H_{16}O_5N_2S$	9 62	9.87

7-sec.-*Aminomethyl-8-hydroxyquinoline-5-sulphonic Acid.*—By following the above procedure with 2.25 g. (0.01 *M*) of 8-hydroxyquinoline-5-sulphonic acid, 0.3 g. (0.01 *M*) of paraformaldehyde and 0.1 *M* of the secondary amines (dimethylamine, diethylamine, di-*n*-propylamine and diethanolamine) the free Mannich bases were obtained. Their m.p., yields and analysis (% sulphur) are shown in Table III (compounds 1-4).

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THE USE OF SOME THIOGLYCOLLANILIDES IN INORGANIC ANALYSIS. PART II

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The use of 9 thioglycollanilides in inorganic analysis has been studied. Precipitates or colour changes were produced with Ag, Pb, Hg^{I}, Hg^{II}, Cu, Cd, Bi, Sn, Zn, Co, Ni and molybdate in most cases. Sensitivity limits for cobalt were found to be 0.5 to 0.25γ with the reagents. Gravimetric estimations of silver with 4 reagents and of cobalt with 3 reagents have been described.

The use of ten new thioglycollanilides in inorganic analysis has been discussed in an earlier paper (this *Journal*, 1955, **32**, 127). Some more thioglycollanilides, derived from simpler aromatic amines, have now been studied from the same point of view, and form the subject matter of the present communication.

Experimental

The compounds were prepared by direct condensation of thioglycollic acid and an aromatic amine in an atmosphere of CO_2, at 110°-120°, by the improved method described earlier in Part I (*loc. cit.*). The amines used were *m*- and *p*-toluidines, *m*-and *p*-chloroanilines, *p*-aminobenzoic acid, *o*- and *m*-anisidines, *p*-nitroaniline and α-naphthylamine. Excepting the toluidine derivatives, which were known previously (Heilbron and Bunbury, 'Dictionary of Organic Compounds', 1943, Vol. III, p. 752), the others are new. The melting points, % sulphur and some physical properties of the compounds are summarised in Table I.

Table I

[M = –(CO.CH_2.SH). sol. = soluble. sp. = sparingly]

Serial No.	Compounds.	M.P.	% Sulphur. Found.	Calc.	Properties.
1.	*m*-M-toluene	150°	17.54	17.68	White, odourless crystal; insol. in water & dil. HCl; sol. in alcohol or acetone.
2.	*p*-M-toluene	125°	17.35	17.68	Do; do
3.	*m*-M-chlorobenzene	75°	15 92	15 87	Do; do, with disagreable odour.
4.	*p*-M-chlorobenzene	126°	16.27	15.87	Do; do, almost odourless.
5.	*p*-M-benzoic acid	221°	15.44	15.17	Do; do, & readily sol. in cold dil. alkalies; liberates CO_2 of $NaHCO_3$ solution.
6.	*o*-M-anisole	65-66°	16.73	16.24	White, odourless crystal; insol. in water or dil. HCl, highly sol. in alcohol or acetone.
7.	*p*-M-anisole	115°	16.15	16.24	White odourless crystal; insol in water or dil. HCl; highly sol. in alcohol or acetone.
8.	*p*-M-nitrobenzene	181°	13.57	15.10	Pale yellow; do do
9.	α-M-naphthalene	180°	15.13	14.74	White powder; insol. in water, or dil. HCl, but sol. in alcohol & acetone.

Use in Qudlitative Analysis

Molar solutions of a soluble salt of Ag, Pb, Hg^{I}, Hg^{II}, Cu^{II}, Cd, Bi, As, Sb, Sn^{II}, Fe^{III}, Al, Cr, Mn, Zn, Co, Ni, Ca, Sr, Ba, Mg, MoO_4^{2-} and WO_4^{2-} were used in the tests. The tests were carried out at different p_H ranges, for which use was made of a series of sodium acetate-acetic acid buffers with p_H 3.42, 4.0, 5.0, 6.0. Tests in neutral solutions were regarded as being carried out at p_H 7. For reactions at higher p_H, ammoniacal solutions of cations, where possible, were used. Same procedure, as described in Part I, was employed for making the tests (*loc. cit.*). The results of the investigation are summarised below.

The *m*-toluidine derivative, at p_H 3.42-7.0, gave light yellow precipitates with Ag and Pb, grey with Hg^{I}, white with Hg^{II} and Cd, pink with Co and at p_H 5-7, a brown precipitate with Ni. The Co and Ni complexes were voluminous precipitates in ammoniacal medium. Molybdate gave a yellow precipitate at p_H 3.42, but the solution turned blue on keeping or heating; at p_H 4-7 the solution turned blue gradually on keeping. All the precipitates, excepting the molybdate complex, were insoluble in dilute alcohol, but the latter was soluble affording a blue solution on heating. The Ag and Hg^{I} complexes were insoluble in dilute acids. The cobalt complex was stable even in cold concentrated acids. Complete precipitation was noted in case of Ag, Hg^{II}, and in ammoniacal solution, of Co.

The *p*-toluidine derivative, at p_H 3.42-7, yielded pale yellow precipitates with Ag and Pb, grey with Hg^{I}, white with Hg^{II}, pink with Co, and at p_H 5-7 brown precipitate with Ni. Molybdate behaved similarly to the above reagent. In ammoniacal medium the Co and Ni complexes were voluminous. The nature of the complexes was almost the same as in the case of the above reagent. Complexes of Ag, Hg^{II}, and in ammoniacal medium, Co appeared quantitative.

The *m*-chloroaniline derivative, at p_H 3.42-7, furnished yellow precipitates with Ag, Pb, Cu and Bi; grey with Hg^{I}; white with Hg^{II} and Cd; pink with Co, and at p_H 5-7 a brown precipitate with Ni. Molybdate behaved as with the above reagents. In ammoniacal medium Co and Ni complexes were voluminous. The silver complex was insoluble in dilute alcohol, dilute HNO_3 and NH_4OH, and did not decompose in boiling water; the complex was soluble in HNO_3 (conc.). The Pb, Hg^{I}, Hg^{II}, Cd, Co and Ni complexes were similar to those of the above reagents. The Bi-complex was partially soluble in hot alcohol and insoluble in cold dilute acids. The Cu-complex was yellowish brown at p_H 4-6; it was not stable; it was partly soluble in alcohol and in hot dilute HCl; in ammoniacal solution a black precipitate, probably of the sulphide, was obtained. Complete precipitation took place in case of Ag, and in ammoniacal medium, of Co.

The *p*-chloroaniline compound, at p_H 3.42-7, gave yellow precipitates with Ag, Pb, and Bi (at p_H 5-6); grey with Hg^{I}; white with Hg^{II} and Cd (at p_H 5-6); pink with Co and brown with Ni (p_H 5-7). Molybdate behaved similarly to the above reagents. In ammoniacal medium Co and Ni gave voluminous precipitates. The nature of the complexes were the same as in in case of the above reagent.

The PABA derivative, at p_H 3.42-7, gave yellow precipitates with Ag and Bi; grey with Hg^{I}; white with Hg^{II}, Cd, Sb, Sn and Zn (at p_H 4-6); greyish brown with Cu,

yellowish grey with Fe^{III}, pink precipitate and colour with Co (p_H 4-6), and brown with Ni (p_H 4-6). In ammoniacal medium Co and Ni produced deep blood-red and brown coloration respectively ; on long standing or on heating partial precipitation of the Co-complex in blood-red colour took place, and the gradually developed Ni-coloration faded slowly. At p_H 3.42 molybdate produced a yellow coloration which on standing gave yellow precipitate; at p_H 4, faint yellow coloration followed by precipitation occurred ; and at these and at p_H 5, 6, 7, blue coloration gradually developed on long standing. The yellow molybdate precipitate on heating or standing turned the solution first green and then blue ; the precipitate was almost insoluble in alcohol. The silver complex turned white on heating. Solubilities of the Ag, Pb, Hg^{I}, Hg^{II} and Bi complexes were similar to the corresponding complexes of the above reagent. The Cu, Cd, Sb, Sn, Fe^{III} and Zn complexes were insoluble in dilute alcohol, but soluble in dilute HCl or HNO_3. The Co and Ni colorations could not be extracted with ether, benzene or amyl alcohol. Complete precipitation took place in case of Ag, Hg^{II}, Cd and Zn (p_H 6).

The *o*-anisidine compound, at p_H 3.42-7, gave yellow precipitates with Ag, Pb and Bi ; grey with Hg^{I} ; white with Hg^{II} and Cd ; yellowish grey with Cu ; pink with Co, and at p_H 4-6, brown with Ni. Molybdate exhibited yellow-blue colour change. In ammoniacal solution Co and Ni gave voluminous precipitates. The Pb and Cu complexes were soluble in hot alcohol. The Ag-complex was not decomposed at the temperature of boiling water and melted with decomposition at 222°. Solubilities of the Ag, Hg^{I}, Hg^{II}, Cd and Bi complexes were the same as the corresponding complexes of the above reagent. The Ni-complex was partly soluble in alcohol and completely in dilute HNO_3 or H_2SO_4. But the Co-complex was resistant to cold HCl (conc.) or HNO_3. The complexes of Ag, Hg^{II} and Co (in ammoniacal solution) were completely precipitated.

The *p*-anisidine derivative, at p_H 3.42-7, gave yellow precipitates with Ag, Pb and Bi; grey with Hg^{I} ; white with Hg^{II} ; pink with Co and brown with Ni (p_H. 4-6). Molybdate behaved similarly as in the above case. In ammoniacal medium Co and Ni complexes were voluminous. The nature of the complexes was the same as in case of the corresponding complexes of the above reagent, but the Pb complex was almost insoluble in dilute alcohol.

The derivative of *p*-nitroaniline, at p_H 3.42-7, produced yellow precipitate with Ag and Pb; grey with Hg^{I}; white with Hg^{II}, Cd and Bi; light brown with Co; brown with Ni (p_H 5-7), and yellow precipitate with MoO_4 (p_H 3.42 4), turning blue on heating or keeping. In ammoniacal medium Co and Ni complexes were voluminous. The silver complex turned brown on heating. Complexes of Ag, Pb, Hg^{I}, Hg^{II}, Cu, Cd, Bi, Co and Ni were insoluble in dilute alcohol ; complexes of Ag and Hg^{I} were insoluble in dilute mineral acids, and the cobalt complex was fairly insoluble in concentrated HCl or HNO_3. Complexes of Ag, Hg^{II} and Co (in ammoniacal solution) were quantitative.

The α-naphthylamine derivative, at p_H 3.42-7, gave yellow precipitates with Ag and Pb; grey with Hg^{I}, white with Hg^{II} and Cd; pink with Co; brown with Ni (p_H 5-7), and yellow-blue colour change with MoO_4. The complexes were insoluble in alcohol. The Ag and Hg^{I} complexes were insoluble in dilute mineral acids, and the

cobalt complex was insoluble even in concentrated HCl or HNO_3. The Ag-complex turned brown on heating. Complete precipitation of Ag and Co (in ammoniacal solution) was noted.

Sensitivity Tests

Sensitivity tests for cobalt with the thioglycollanilides were carried out as the pink colour of the complexes was very dark. Ammoniacal solution was chosen as the test medium, since the complexes were voluminously precipitated from such medium. Solutions of $CoCl_2,2H_2O$ (E. Merck, analytical grade) were prepared in the ammoniacal test medium (a solution containing 2% NH_4Cl and 2*N*-NH_4OH), the concentrations of cobalt being, $1:10^3$, $1:10^4$, $1:10^5$, $1:10^{5\cdot3}$, $1:10^{5\cdot6}$, $1:10^{5\cdot7}$, $1:10^6$, $1:10^{6\cdot3}$, $1:10^7$ respectively ; 1 c.c. each from these solutions was treated with 2 drops of a freshly prepared 1% solution of the reagent. The resulting colour changes and precipitations were noted in cold and on warming. In some cases the coloration produced was found to be adsorbed on the reagent that usually came down due to dilution of the alcoholic solution. Almost in all cases the precipitation limit fell between cobalt concentration $1:10^3$ and $1:10^4$. Table II records the limiting concentrations for identification of cobalt with the respective reagents. The limit of identification (in γ) has been obtained from filter paper spot test, in which a drop of cobalt solution of definite concentration was added to a filter paper ; the paper was dried, a drop of the reagent solution was added over the spot, and the the paper was held over the mouth of a bottle of ammonia.

TABLE II

Sl. No. of reagents ...	1	2	3	4	5	6	7	8	9
Limiting conc. $=10^{-x}$, where x=	6.0	5.7	6.3	5.7	5.0	5.3	5.3	5.6	5.0
Identification limits (in γ) ...	0.05	0.25	0.05	0.25	0.50	0.50	0.50	0.25	0.50

Use in the Gravimetric Analysis

Some of the thioglycollanilides were used in gravimetric estimations of Ag and Co, since qualitative analysis indicated complete removal of these cations from their solutions by the reagents.

Silver Complexes.—Silver formed yellow complexes with the thioglycollanilides, which were, in general, precipitated completely from a solution of $AgNO_3$ in slightly acidic medium. Some of these complexes were not decomposed when heated on a water-bath, and attempt was made to ascertain their applicability in silver estimation. The reagents used were *o*-(mercaptoacetamido)-anisole, *m*- and *p*-(mercaptoacetamido)-chlorobenzenes and *p*-(mercaptoacetamido)-toluene.

The complexes were precipitated by addition of an 1% alcoholic solution of the respective reagent to a hot $AgNO_3$ solution, the mixture being digested on a water-bath for about half to one hour, filtered, washed free from excess of the reagent by hot dilute alcohol, and dried at 100°-110°. A known weight of the dried complex

was then ignited in a porcelain crucible and weighed as metallic silver. From this the %Ag in the complexes was calculated. Table III records the %silver and the assumed composition of the complexes.

TABLE III

(% Ag found is the mean of 3 expts.)

Sl. No. of reagent.	Assumed composition.	% Silver. Found.	Calc.
2.	[*(p)* $CH_3.C_6H_4.NH.CO.CH_2S$] Ag, $2H_2O$	33.92	33.31
3.	[*(m)* Cl $C_6H_4.NH.CO.CH_2S$] Ag	34.90	34.78
4.	[*(p)* $Cl.C_6H_4.NH.CO.CH_2S$] Ag	34.88	34.78
6.	[*(o)* $OCH_3.C_6H_4.NH.CO.CH_2S$] Ag	35.40	35.49

In gravimetric determination of the metal by direct weighing of the complexes the above assumed compositions were taken into account.

For estimation, 10 c.c. of a standard $N/10$-$AgNO_3$ solution was pipetted out, diluted to 100 c.c., acidified with 4 drops of HNO_3 (conc.), and was heated to gentle boiling. To this hot solution a freshly prepared 1% alcoholic solution of the organic reagent was added from a pipette slowly with constant stirring till precipitation appeared to be complete. In case of the methoxy compound, under the above conditions the precipitate began to coagulate as the equivalence point aproached. The precipitate was digested on a water-bath for about ½ hour when complete coagulation took place. Complete precipitation was ensured by addition of a further small amount of the precipitant, and digestion was continued for about one hour more. The content was cooled and allowed to stand at room temperature for several minutes. The precipitate was filtered through a weighed G_4-crucible, washed free from excess of the reagent by hot water in all the cases, and finally dried at 100°-110° to a constant weight. The results of estimations are recorded in Table IV.

TABLE IV

Ag taken = 0.1082 g. Drying temp. = 100°–110°.

Wt. of complexes.	Ag found.	Wt. of complexes.	Ag found.	Wt. of complexes.	Ag found.	Wt. of complexes	Ag found.
Reagent No.2.		Reagent No.3.		Reagent No.4.		Reagent No.6.	
0.3198 g.	0.1065 g.	0.3076 g.	0.1076 g.	0.3106 g.	0.1080 g.	0.3066 g.	0.1088 g.
0.3208	0.1069	0 3078	0.1076	0 3106	0.1080	0.3056	0.1085
0.3198	0.1065	0.3072	0.1074	0.3100	0.1079	0.3060	0.1086
0.3204	0.1067						

Cobalt Complexes.—The thioglycollanilides form dark pink complexes with cobalt which are voluminously precipitated from a faintly ammoniacal solution. It has been shown earlier that these are cobaltic complexes (*loc. cit.*), and the same procedure for estimation of cobalt has been employed in the present investigation.

The reagents used were *p*-(mercaptoacetamido)-chlorobenzene, *o*-(mercaptoacetamido)-anisole and *p*-(mercaptoacetamido)-toluene. The former two reagents provided fairly reproducible results when the complexes were directly weighed as such, but the latter afforded variable results in such methods. The chloro compound gave 0.3503 g. of complex at 110° drying temperature (mean of 3 experiments) from 10 c.c. of the solution, indicating the amount of cobalt to be 0.03125 g. against 0.03163 g. The methoxy compound gave 0.3434 g. complex at 100°, indicating 0.03126 g. of Co against 0.03163 g. from the same solution. The composition of the complexes assumed in the above calculation corresponds to the cobaltic complexes having no associated water molecules. The complex obtained in case of the *p*-(mercaptoacetamido)-toluene from 10 c.c. of the standard solution was filtered through an ashless (Whatman No. 42) filter paper, washed several times with warm water till free of chloride (since NH_4Cl was added to the solution in the precipitation process), dried, ignited to Co_3O_4 in a porcelain crucible, and hence, the amount of cobalt was calculated. By this process cobalt found was 0.03158 g. against 0.03163 g.

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COLORIMETRIC ESTIMATION OF IRON BY DIPHENYLTHIO-VIOLURIC ACID

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Diphenylthiovioluric acid has been used for the colorimetric estimation of iron in the ferrous state in a photoelectric colorimeter. The maximum absorption due to the coloured complex is in the region of 660 mμ. The estimation of iron can be accurately carried out when the concentration is between 0.2 and 1.2 parts per million parts of the solvent. The effect of various ions and other factors on the coloured complex has also been studied.

Preparation of complexes of diphenylthiovioluric acid with many metals was reported by Ghambhir and Singh (*Proc. Ind. Acad. Sci.*, 1946, **23A**, 330). It was found that ferrous iron formed a deep blue insoluble complex which was precipitated on addition of a solution of the ammonium salt of diphenylthiovioluric acid to an aqueous solution of a ferrous salt.

The complex dissolves in acetone or in aqueous acetone, forming a deep bluish green solution. A large excess of the reagent is needed for full development of colour. Maximum absorption due to the coloured complex takes place in the region of 660 mμ, and this region remains unaltered by an excess of the reagent. Full development of colour is instantaneous and the intensity of colour remains constant for several days. For these estimations, iron must be in the ferrous state, and if it is in the ferric condition, it can be reduced by hydroquinone, an excess of which does not interfere. It was found that several cations and anions had no effect on the colour intensity, but some interfered.

Experimental

The optical density measurements were carried out with a Klett-Summerson photoelectric colorimeter, of which the scale reading was directly proportional to the optical density of the coloured solution as determined by the photo-electric cell. Since the optical density is proportional to the concentration of the coloured substance (Beer's law), the scale readings are therefore proportional to the concentration of the substance under examination.

The chemicals used were all of the reagent quality. Standard solutions of iron were prepared from ferrous ammonium sulphate (A.R., B.D.H.) and the iron content was checked volumetrically by titrating against standard potassium permanganate.

Instead of using the ammonium salt of diphenylthiovioluric acid, it was found that the acid itself could be used. Solutions of diphenylthiovioluric acid were prepared in acetone (0.5%). Standard solutions of various ions were prepared from nitrates, sulphates or chlorides in the case of cations, and from the sodium or potassium salts in the case of anions.

Region of Maximum Absorption.—A standard solution (5 c.c.) of Mohr's salt containing an appropriate quantity of iron was taken for each estimation and 5 c.c. of acetone solution of diphenylthiovioluric acid containing an excess of the reagent was added to it. The acetone concentration in the final solutions was maintained at 50% throughout to facilitate comparison.

The bluish green colour, formed by the reagent with iron in 50% acetone solution, showed maximum absorption in the region of 660 mμ. Varying amounts of iron and the reagent had no influence on the region of maximum absorption. The observations are recorded in Table I.

TABLE I

Wave-length (mμ) ...	490	515	550	575	595	640	660
		Fe^{2+} soln. = 4 p.p.m.					
Col. readings ...	380	305	320	390	450	340	280
		Fe^{2+} soln. = $_2$ p.p.m.					
Col. readings ...	270	190	165	195	240	222	143

Effect of Reagent.—It was found that a large excess of the reagent was necessary for full colour development, due probably to the reversibility of the reaction :

$$Fe^{2+} + 2RH = Fe(R)_2 + 2H^+.$$

From the observations, recorded in Table II, it will be seen that about 200 times the theoretical quantity of the reagent is necessary for full colour development. Even larger quantities of the reagent do not interfere.

TABLE II

Reagent soln. taken (in c.c.)	1	2	3	4	5	6
Col. readings for Fe^{2+} soln. = 2 p.p.m.	45	72	98	142	143	143
Col. readings for Fe^{2+} soln. = 1 p.p.m.	27	52	73	73	73	73

Beer's Law.—That Beer's law is obeyed by the colour system is shown by the fact that the colorimetric readings are directly proportional to the amount of iron present in the solution, as shown by the observations recorded in Table III. The iron content of the solution should be between 0.1 and 1.2 μg./c.c. In case the amount of iron is more than this limit, Beer's law is obeyed only approximately.

TABLE III

Iron soln. taken (in c.c.)	1	2	3	4	5
Col readings for Fe^{2+} soln. = 2 p.p.m.	30	60	88	116	145
Col. readings for Fe^{2+} soln. = 4 p.p.m.	61	117	175	226	282

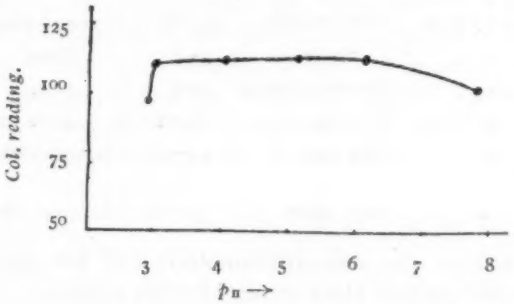
Effect of Time and Temperature on the Coloured System.—Full colour development took place immediately after the addition of the reagent. The absorption due to the coloured system was found to remain constant for days together for concentrations

of iron greater than 0.2 p.p.m. The ratio of acetone and water in the final solutions was maintained at 50 : 50. Experiments were carried out with solutions of concentrations of 4 p.p.m. and 2 p.p.m., keeping the quantity of the reagent solution the same in both cases (5 c.c. of 1% soln.). The coloured complex in solution was exposed to diffused day light and readings were taken after an interval of 10 minutes. The readings were found to be constant for two days, after which no readings were taken.

As regards the effect of temperature, it was found that a change between 10° and 50° did not alter the colorimetric readings.

Effect of Change of p_H on the Colour System.—Very dilute solutions of Merck's pure HCl and NaOH were prepared to study the effect of variation of p_H on the colour system. The concentrations of iron and the reagent and the proportions of acetone and water in the final solutions were kept constant throughout. The results are graphically reprsented in Fig. 1.

FIG. 1



From the above figure, it can be seen that the p_H of the solution must be adjusted between 3.1 and 6.0 for correct estimations.

Effect of Reducing Agents.—As already pointed out, iron must be in the ferrous state for these estimations. The effect of reducing agents on the colour system was therefore studied. It was found that hydroquinone worked best for reduction of iron. The quantity of hydroquinone must be at least 50 times the quantity of iron present for complete reduction so that the full colour development may take place. A much larger quantity of hydroquinone can, however, be tolerated.

Reduction of iron with hydroxylamine hydrochloride or hydrazine hydrochloride was also carried out, but the solution became acidic, and p_H of the solutions had to be adjusted within the required limits. Detailed investigations with these reducing agents were not carried out.

Effect of various Anions.—The effect of various anions on the colour system was studied by the addition of sodium or potassium salt of the corresponding ion in different quantities before measuring the colour density. It was found that chloride, bromide, iodide, nitrate, nitrite, sulphate and thiocyanate did not interfere even if present in relatively large quantities (as much as 100 times the quantity of iron). On the other hand, oxalate, citrate and tartrate interfered even if present in small quantities. The measurements were carried out under appropriate conditions, discussed above.

Effect of various Cations.—The effect of different cations was similarly studied by adding soluble salts of the metals to the iron solution. It was found that ions of the alkali and alkaline earth metals caused no interference even at relatively high concentrations (as much as 500 p.p.m. for 2 p.p.m. of iron), whereas those of copper, silver and gold showed marked interference. Copper cannot be tolerated at all; silver can be tolerated up to 10 p.p.m. and gold up to 20 p.p.m. Aluminium and chromium can be tolerated up to 20 and 40 p.p.m. respectively, whereas nickel, zinc, lead, mercury, stannic, manganese and magnesium can be tolerated even up to concentrations of 100 times that of iron.

Comparison with other Reagents.—The characteristics of common colorimetric reagents for iron have been compared with those of diphenylthiovioluric acid in Table IV.

TABLE IV

Reagent.	Sensitivity.	Stability of colour.	p_H range.	Effect of excess.	Beer's law.
KCNS	1 p.p.m.	Fades rapidly	0.05-1*N*	Increases intensity	Slight deviation.
Dipyridyl	1	1 year	3–9	None	Obeyed.
o-Phenanthroline	2	6 months or more	2–9	None	Do
Salicylaldoxime	4	1 day	6.2–6.6	None	Do
Salicylic acid	12	2-3 days	2.5–2.7	Increases intensity	Do
Diphenylthio-violuric acid	0.2	Very stable	3.1–6.0	Increases intensity	Do

The above table shows that diphenylthiovioluric acid has many advantages over some of the well known reagents which are used for this purpose.

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EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART VII. 1 : 2-BENZODIPHENYLENE OXIDE

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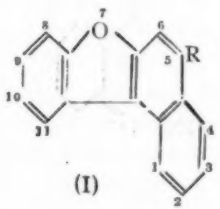
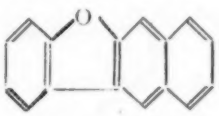
Two unequivocal syntheses of 1 : 2-benzodiphenylene oxide (γ-brazan) are recorded, proving the earlier descriptions of the compound in the literature as incorrect.

Derivatives of 1 : 2-benzodiphenylene oxide (γ-brazan*) (I), such as α-anhydrotrimethylbrazilone and allied products, have been synthesised by Johnson and Robertson (*J. Chem. Soc.*, 1950, 2381; also cf. Chatterjea, this *Journal*, 1953, **30**, 103). There is discrepancy in the literature with regard to the parent compound (I). Graebe and Arx claimed to have prepared this compound by heating a mixture of β-naphthol and phenol with litharge and reported the m.p. 296° (*Annalen*, 1881, **209**, 145). Sabatier and Mailhe (*Compt. rend.*, 1912, **155**, 202) obtained a product, m.p. 200°, by heating a mixture of β-naphthol and phenol over thorium oxide and formulated it as either γ-(I) or β-brazan (II). But as the latter (m.p. 208°) did not produce the colour reactions described by Sabatier and Mailhe (*loc. cit.*) for the above product (Kostanecki and Lloyd, *Ber.*, 1903, **36**, 2193), it appeared likely that they had really obtained (I). It was therefore desirable to resolve this obvious discrepancy.



(I)

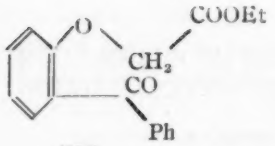


(II)

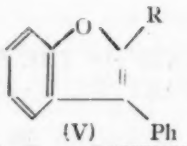
[I : R = H;
III : R = OH;
VI : R = COOH]

By an adaptation of the method of Johnson and Robertson (*loc. cit.*), the 5-hydroxy-γ-brazan (III) has been prepared from 2-hydroxybenzophenone. The latter was converted into ethyl 2-benzoylphenoxyacetate (IV) and then cyclised with sodium ethoxide in alcohol to ethyl 3-phenylcoumarone-2-carboxylate (V : R = CO_2Et). The corresponding acid (V : R = CO_2H) on homologation by the Arndt-Eistert procedure afforded 3-phenylcoumarone-2-acetic acid (V : R = CH_2COOH), isolated by way of the amide. On cyclisation with phosphoric anhydride in benzene, a quantitative yield of the α-naphthol (III) was obtained. The phenol on reduction with hydriodic acid furnished a poor yield of γ-brazan which was obtained as a low-melting solid (m.p. 31-32°), characterised by a well-crystalline picrate.

* Benzo[b]naphtho [1.2-d] furan (I) is termed γ-brazan and 3 : 4-benzodiphenylene oxide (benzo-[b] naphtho [2.1-d] furan) is termed α-brazan (Patterson and Capell, "The Ring Index", Reinhold, Ring System No : 2483 and 2482 respectively).



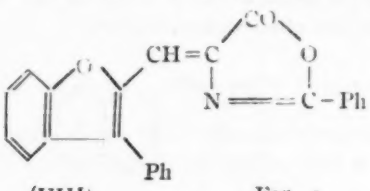
(IV)



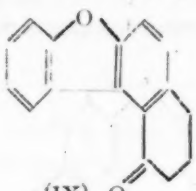
(V)

(VII : R = CONHNH
SO_2PH)

A better route to γ-brazan was from 2-formyl-3-phenylcoumarone (V : R = CHO) which was obtained in poor yield by the Gattermann synthesis from 3-phenylcoumarone (V : R = H), prepared conveniently by the action of sodium acetate and acetic anhydride on the acid (IV : H in place of Et). The aldehyde was, however, obtained in quantity from the corresponding acid by the Stevens-McFadyen method involving the decomposition of the sulphonhydrazide (VII) with sodium carbonate in ethyleneglycol (*J. Chem. Soc.*, 1936, 584). The azlactone (VIII), derived from the aldehyde, afforded the pyruvic acid (V : R = $CH_2CO.COOH$), isolated by the sulphur dioxide method. It underwent cyclisation in quantitative yield to the acid (VI) with hydrobromic acid in acetic acid. On decarboxylation with the aid of lime, this acid afforded γ-brazan, identical with the product, mentioned above.

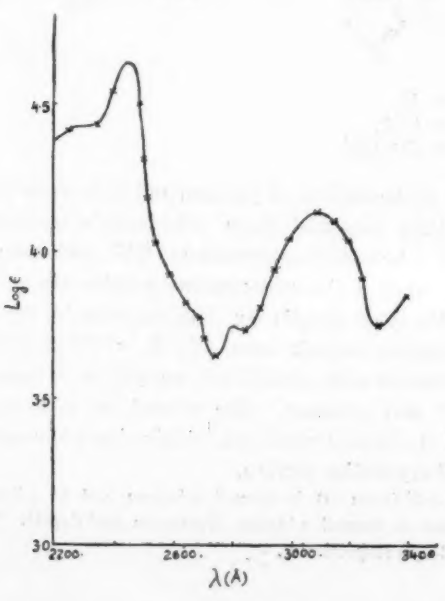


(VIII)



(IX)

FIG. 1



It is clear from the above work that the products of Graebe and of Sabatier must have different constitutions and this was further confirmed by an independent synthesis of γ-brazan from the cyclic ketone (IX), described earlier (Mosettig and Robinson, *J. Amer. Chem. Soc.*, 1939, **61**, 1148; Chatterjea, *loc. cit.*). γ-Brazan was obtained from this ketone either by reduction with lithium aluminium hydride to the corresponding carbinol, followed by treatment with palladised charcoal or by the Wolff-Kishner reduction to the tetrahydro-γ-brazan, followed by dehydrogenation with selenium. The absorption spectrum of (I) is shown in Fig. 1.

EXPERIMENTAL*

3-Phenylcoumarone-2-carboxylic Acid.—A mixture of 2-hydroxybenzophenone (5 g.), ethyl bromoacetate (5 c.c.) and dry potassium carbonate (12 g.) in dry acetone (40 c.c.) was refluxed for 8 hours. Isolated as usual, the resulting phenoxyacetic ester was obtained as a light brown oil (negative ferric reaction) which was heated in vacuum at 180° to remove all volatile impurities. The crude ester was cyclised by adding a solution of the compound in dry alcohol (15 c.c.) to a solution of alcoholic sodium ethoxide (Na, 0.5 g. in alcohol, 35 c.c.) and refluxing the mixture for 1 hour. The mixture was then poured into cooled water when *ethyl 3-phenylcoumarone-2-carboxylate* separated as an oil, which easily solidified, yield 3 g. The ester crystallised from alcohol in prisms, m.p. 64° and developed a pinkish red coloration with H_2SO_4. (Found: C, 76.0; H, 5.5. $C_{17}H_{14}O_3$ requires C, 76.6; H, 5.3 per cent). The alkaline filtrate, after removal of alcohol, on acidification furnished 3-phenylcoumarone-2-carboxylic acid (0.3 g.). This acid was prepared from the above ester (3 g.) by hydrolysing with alcoholic sodium hydroxide (40 c.c., 10%) for ½ hour on a boiling water-bath. On acidification, the acid was obtained which crystallised from acetic acid in yellowish needles (2.1 g.), m.p. 234° (Fuson *et al.*, *J. Org. Chem.*, 1941, **6**, 845, report m.p. 232-33° for the same compound obtained by a different method). The compound dissolved in sulphuric acid with a yellow colour which became pinkish on warming.

3-Phenylcoumarone.—The crude ethyl 2-benzoylphenoxyacetate, obtained in the above preparation, on hydrolysis afforded the corresponding acid as an oil which was isolated with ether. This phenoxy-acid (5 g.) was dissolved in acetic anhydride (40 c.c.), anhydrous sodium acetate (8 g.) was added and the mixture heated on an oil-bath at 165° for ½ hour. After the brisk reaction was over, the mixture was added to water (50 c.c.), extracted with ether and the ethereal layer washed several times with sodium bicarbonate solution. On removal of the ether, 3-phenylcoumarone (2.9 g.) was obtained as an oil which solidified, m.p. 42° (Stormer and Kippe, *Ber.*, 1903, **36**, 4005, record m.p. 42°). The compound developed an orange-yellow coloration with H_2SO_4. (Found: C, 86.4; H, 5.4. Calc. for $C_{14}H_{10}O$: C, 86.6; H, 5.2 per cent).

* All m.p.'s are uncorrected.

3-Phenylcoumarone-2 acetic Acid.—(*a*). The acid (V : R = COOH) (3.0 g.) was converted into the acid chloride by boiling in thiophene-free benzene (10 c.c.) with purified thionyl chloride (6 c.c.). The colorless crystalline acid chloride, obtained on removal of benzene and volatile impurities in vacuum, was dissolved in benzene (10 c.c.) and added dropwise to a solution of diazomethane (from nitrosomethylurea, 12 g.) in ether (120 c.c.) at 0°. The next day the solution was filtered and the solvent removed in vacuum. The diazo-ketone (3.0 g.) crystallised from benzene-petroleum ether in yellow prisms, m.p. 112-14° (decomp.). (Found : N, 11.0. $C_{16}H_{10}O_2N_2$ requires N, 10.7 per cent). A solution of the diazo-ketone (2.9 g.) in purified dioxan (70 c.c.) was added during ½ hour to a stirred solution of silver nitrate (40 c c., 10%) in concentrated aqueous ammonium hydroxide (30 c.c.) at 70°. After heating on a water-bath for 3 hours, the mixture was left overnight, filtered and poured into a large volume of water. The crude 3-phenylcoumarone-2-acetamide was collected and hydrolysed with aqueous alcoholic potash (30 c.c., 10%) for 5 hours. After removal of the alcohol, the cooled residue was diluted with water, clarified with charcoal, filtered and acidified to afford the *acid* (V : R = CH_2COOH) (2.6 g.), crystallising from benzene-light petroleum in cream-coloured needles, m.p. 146°. (Found: C, 76.0 ; H, 5.0. $C_{16}H_{12}O_3$ requires C, 76.2 ; H, 4.7 per cent).

The compound dissolved in H_2SO_4 with an orange-yellow colour, turning green slowly with the appearance of a violet fluorescence. The acid also exhibited a violet fluorescence in acetic acid. The *p-toluidide* crystallised from acetic acid in colorless needles, m.p. 183°. (Found : C, 81.2 ; H, 5.8. $C_{23}H_{19}O_2N$ requires C, 80.9 ; H, 5.6 per cent).

(*b*). The pyruvic acid (V : R = $CH_2CO.COOH$) (0.3 g., *vide infra*) was dissolved in dilute NaOH solution (5 c.c., 5%), cooled to 5° and treated with perhydrol (0.6 c.c., 30%) during 5 minutes. After leaving for 2 hours, the mixture was acidified to yield the acid (V : R = CH_2COOH) (0.2 g.) as cream-coloured needles, m.p. 145-46° (from acetic acid).

Cyclisation of 3-Phenylcoumarone-2-acetic Acid.—The acid (1.2 g.) was dissolved in benzene (45 c. c.) and treated with constant stirring with P_2O_5 (7.2 g.) and refluxed for 4 hours. The mixture was then decomposed with ice and the benzene layer washed several times with sodium carbonate solution. On removal of benzene the phenol, *5-hydroxy-γ-brazan* (III) was obtained (0.75 g.) which crystallised from acetic acid in cream-coloured prisms, m.p. 142°. (Found : C, 82.0 ; H, 4.4. $C_{16}H_{10}O_2$ requires C, 82.1 ; H, 4.3 per cent).

γ-Brazan.—The above α-naphthol (0.5 g.) was boiled with freshly distilled hydriodic acid (5 c. c.) for 8 hours. The mixture was extracted with ether, washed with sodium thiosulphate solution, dried (sodium sulphate) and distilled in vacuum at 180° (bath temp.). The mobile distillate furnished a crystalline picrate (0.08 g.) which crystallised from alcohol in orange needles, m.p. 124°. (Found : C, 59.5 ; H, 3.2 ; N, 9.4. $C_{16}H_{10}O.C_6H_3O_7N_3$ requires C, 59.1 ; H, 2.9 ; N, 9.4 per cent). γ-Brazan, liberated from the picrate by alkali, was obtained as a liquid which solidified on keeping, m.p. 31-32°. (Found : C, 88.3 ; H, 4.6. $C_{16}H_{10}O$ requires C, 88.1 ; H, 4.6 per cent). The compound showed with H_2SO_4 the following successive changes in colour: blue → deep blue → green → pinkish → yellowish green.

U.V. absorption (Fig.1) : $\lambda_{max}^{alcohol}$, 2450 Å (log ϵ, 4.64), 2800Å (log ϵ, 3.74), 3100Å (log ϵ, 4.13).

The residual glassy material in the distilling flask in the above experiment solidified on trituration with acetone and was obtained as a greenish yellow mass, m.p. 246°. This was not investigated.

Attempt to prepare γ-Brazanquinone * *by oxidation of 5-Hydroxy-γ-brazan.*—The phenol (0.4 g.) was dissolved in acetic acid (10 c. c.) and to the boiling solution was added a solution of chromic acid (0.38 g.) in water (3 c.c.). After boiling for 5 minutes the mixture was poured into water. The deep orange-red resinous mass (0.1 g.) separating was a mixture of quinones (the colour was rapidly discharged on reduction with zinc dust in acetic acid). On attempting to isolate γ-brazanquinone as the azine, the above mixture was boiled with *o*-phenylenediamine (0.1 g.) in acetic acid (6 c.c.). An unidentified product, m.p. 245° (from acetic acid), was deposited as brownish prisms (20 mg.), developing a yellowish green coloration with H_2SO_4. (Found : C, 78.5 ; H, 4.3 ; N, 0.0 per cent).

2-Formyl-3-phenylcoumarone.—(*a*). To a solution of 3-phenylcoumarone (2.8 g.) in ether (80 c. c.) fused zinc chloride (1.2 g.) and anhydrous hydrogen cyanide (4 c.c.) were added and the mixture saturated with hydrogen chloride at 0°. The next day the crystalline product separating was collected, washed with dry ether, treated with water (50 c.c.) and heated on a water-bath for ½ hour. The oil (0.2 g) separating was isolated with ether. The aldehyde did not crystallise. It dissolved in H_2SO_4 with a yellowish colour, turning green.

The *semicarbazone* crystallised from alcohol in cream-coloured needles, m.p. 246-48°. (Found : C, 68.7 ; H. 5.0. $C_{16}H_{13}O_2N_3$ requires C, 68.8 ; H, 4.7 per cent).

The *2:4-dinitrophenylhydrazone*, prepared in alcohol with the aid of HCl, was obtained in two forms : (*i*) Dark red leaflets with a steel-blue reflex, m.p. 264° (from acetic acid. (Found : N, 14.1. $C_{21}H_{14}O_5N_4$ requires N, 13.9 per cent). (*ii*) Orange-yellow needles, m.p. 234° clearing at 260° (from acetic acid). (Found : N, 13.8. $C_{21}H_{14}O_5N_4$ requires N, 13.9 per cent).

(*b*). *From 3-Phenylcoumarone-2-carboxylic Acid.*—This acid was esterified with diazomethane yielding the *methyl ester* which crystallised from methyl alcohol in cream-colored prisms, m. p. 97°. (Found : C, 76.3 ; 5.0. $C_{16}H_{12}O_3$ requires C, 76.2 ; H, 4.7 per cent). A mixture of the ester (1 g.), hydrazine hydrate (2 c. c., 90%) and ethyl alcohol (3 c.c.) was boiled under reflux for 5½ hours and then poured into water. The *hydrazide* ($V:R=CONHNH_2$) (0.9 g) was obtained as a crystalline solid, crystallising from methanol in colorless long needles, m.p. 79-80°. (Found : N, 11.5. $C_{15}H_{12}O_2N_2$ requires N, 11.1 per cent). The *picrate* crystallised from alcohol in yellow prismatic needles, m.p. 195° (decomp.).

A solution of the hydrazide (1.5 g.) in dry purified pyridine (10 c. c.) was cooled to 0° and treated dropwise with benzenesulphonyl chloride (0.9 g.). The solution turned yellow and after sometime yellowish needles began to separate. The mixture was kept in a refrigerator for 6 hours and then poured into iced HCl. The gummy yellow mass

* Also named α-brazanquinone.

of the *sulphonhydrazide* (VII) (quantitative yield) solidified easily and was obtained in colorless prisms from methanol, m.p. 233-34° (decomp.). (Found: N, 6.8. $C_{21}H_{16}O_4N_2S$ requires N, 7.1 per cent).

A solution of the sulphonhydrazide (0.4 g.) in ethyleneglycol (3 c.c.) at 160° was treated with anhydrous sodium carbonate (0.4 g., added in one lot). A vigorous evolution of gas took place and after 80 seconds the reaction was quenched by pouring the mixture into hot water which was then cooled and the oily aldehyde (0.15 g.) was extracted with ether.

3-Phenylcoumarone-2-pyruvic Acid.—The crude aldehyde (3.0 g.) was converted into the *azlactone* (VIII) by heating on a boiling water-bath with a mixture of hippuric acid (2.0 g.), fused sodium acetate (1 g.) and acetic anhydride (20 c.c.) for 20 minutes. Dilute alcohol (40 c. c., 50%) was then added to the mixture and the crystalline material collected after 2 hours, washed with boiling water and then with cold alcohol. The azlactone (3.4 g.) crystallised from benzene in orange-yellow needles, m.p. 240-42°. (Found : C, 79.4 ; H, 4.5. $C_{24}H_{15}O_3N$ requires C, 78.9 ; H, 4.1 per cent).

The azlactone (2.5 g.) was boiled under reflux with KOH (35 c.c., 10%) for 4½ hours. An oily product separated. The mixture was filtered, cooled, diluted with water (30 c.c.) and saturated with SO_2 at 25°. The *pyruvic acid* (V: R = $CH_2CO.COOH$) was isolated in the usual manner. It crystallised from acetic acid as a colorless powder (0.4 g.), m. p. 242-44° showing a violet ferric reaction. (Found : C, 72.2; H, 4.6. $C_{17}H_{12}O_4$ requires C, 72.8; H, 4.3 per cent). The compound developed a yellowish green coloration with H_2SO_4.

Cyclisation of the Pyruvic Acid.—The foregoing ketonic acid (0.3 g.) was dissolved in acetic acid (3 c.c.) and boiled under reflux with HBr (2 c.c., 48%) for 3 hours. On cooling, *γ-brazan-5-carboxylic acid* (VI) separated, crystallising from acetic acid in colorless slender needles, m. p. 290°, yield 0.22 g. (Found : C, 77.4 ; H, 3.9. $C_{17}H_{10}O_3$ requires C, 77.9; H, 3.8 per cent).

The *methyl ester*, obtained by the action of diazomethane, crystallised from methanol in colorless needles, m.p. 101°. (Found : C, 78.2 ; H, 4.8. $C_{18}H_{12}O_3$ requires C, 78.3 ; H, 4.4 per cent).

γ-Brazan.—(*i*). The decarboxylation of the above acid was carried out by mixing with 3 times its weight of lime and heating in a horizontal tube. The γ-brazan distilled as a colorless oil, yielding a crystalline picrate, m.p. 123-24°, undepressed on admixture with the specimen obtained before.

(*ii*) (*a*).—A solution of *1-keto-1:2:3:4-tetrahydro-γ-brazan* (IX, 0.1 g.) in ether (5 c.c.) was treated with the usual precautions with lithium aluminium hydride (50 mg.) and left for 1 hour. The mixture was carefully decomposed with dilute acid, the ethereal layer worked up to give the corresponding carbinol, *1-hydroxy-1 : 2 : 3 : 4-tetrahydro-γ-brazan*, as colorless prisms, m.p. 105-106°. (Found : C, 80.1 ; H, 6.0. $C_{16}H_{14}O_2$ requires C, 80.7 ; H, 5.9 per cent). This carbinol (60 mg.) was mixed with palladised charcoal (50 mg.) and heated at 300° for 3 hours. The resulting violet fluorescing oil was taken up in ether and obtained from low-boiling petroleum ether in colorless prisms, m.p. 31-32° (picrate, m.p. 123-24°), identical with the specimen of γ-brazan obtained above.

(ii) (b).—The ketone (IX, 1.0 g.) was heated in a sealed tube with hydrazine hydrate (1 c.c., 100%) and alcoholic sodium ethoxide (0.5 g. of sodium in absolute alcohol, 10 c.c.) at 180°-190° for 8 hours. The oily product was distilled in an oil pump affording the reduced product as a colorless oil (0.3 g.) which did not solidify on keeping. It was mixed with selenium (1.0 g.) and heated at 300° for 2 hours. The resulting oily product was dissolved in alcohol (10 c. c.), filtered and treated with picric acid. The picrate of γ-brazan separated ; it was collected and crystallised from alcohol in orange needles, m.p. and mixed m.p. 123-24°, yield 0.12 g.

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SETTING OF THE GELS OF SODIUM OLEATE AND STEARATE IN SOME ORGANIC SOLVENTS. PART II. COOLING CURVES OF SOAP-SOLVENT SYSTEMS

By K. B. Deshpande and K. P. Buch

The study of the cooling curves of the solutions of sodium oleate and sodium stearate in nujol has shown that heat is evolved during gelation. The heat of gelation has been calculated for gels of different concentrations under various rates of cooling. It has been observed that the values of the ratio of the heat of gelation per gram molecule of soap to the temperature of setting in absolute units are very nearly constant independent of the rate of cooling and the concentration of the soap.

The cooling curves for solutions of some soaps in water-alcohol mixtures and nujol (Fisher, *Kolloid Z.*, 1929, **46**, 359; Lederer, *ibid.*, 1931, **57**, 116; Lawrence, *Trans. Faraday Soc.*, 1938, **34**, 660) and pinene (Prasad *et al.*, *Proc. Ind. Acad. Sci.*, 1945, **21A**, 1; *J. Univ. Bombay*, 1946, **14**, Part III, 23) have been studied systematically. It has been observed that in all cases heat is evolved at the point of setting of gels, and it is of the same order of magnitude as the heat evolved during solvation of soaps to alco-sols and hydro-sols [Prasad *et al.*, *loc. cit.*, Lederer, *loc. cit.*, Kandelaki, *Khim. Ref. Zhur*, 1941, **4** (6), 18; Izvestiya Gruzinskogo Ind. Inst. Kerova, 13, 109).

Prasad *et al.* (*loc. cit.*) also calculated from the cooling curves the specific heats of the gel-forming solutions just before and after gelation, and found that for the same concentration of soap, the specific heat of the sol state was greater than that of the corresponding gel, and that with the increase in the soap content of the systems, the specific heats in two states also increased.

However, all these observations do not include sufficient exhaustive data regarding the behaviour of any one of the systems under different conditions so as to point out definitely whether or not the process of gelation is comparable to the change of state. In order to study in detail the thermal change accompanying the process of gelation, the cooling curves of solutions of sodium oleate and stearate in nujol have been studied, and the observed results interpreted on theoretical basis.

Experimental

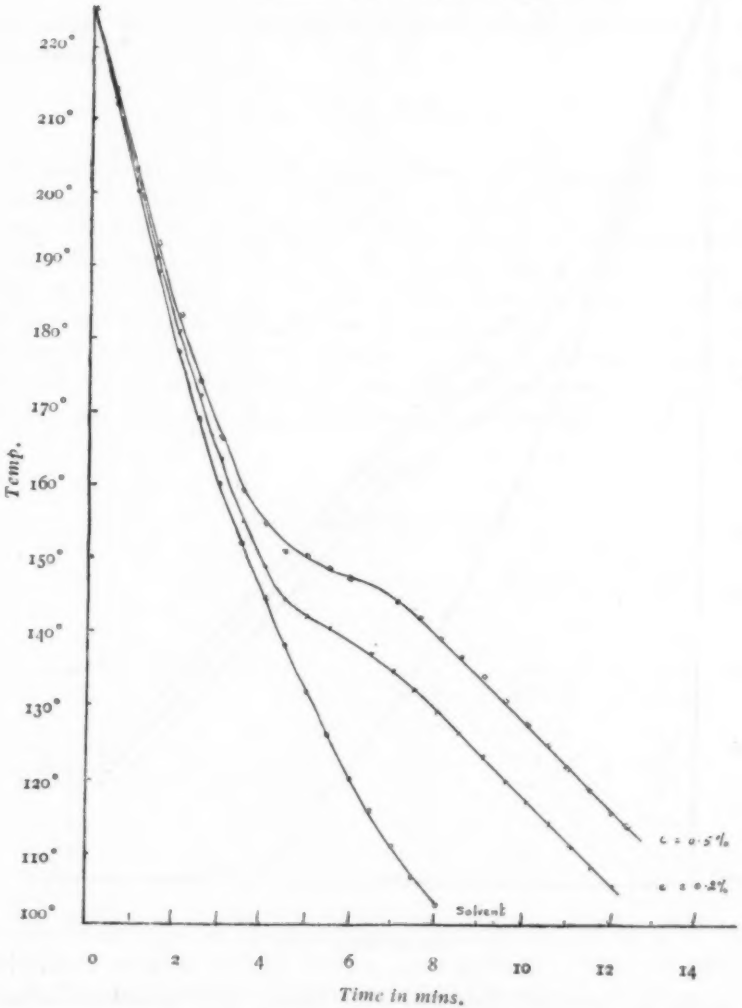
Materials and the mode of preparation of gels used in this investigation are the same as those described in Part I of the series (this *issue*, p. 321).

The cooling curves of the several systems of sodium oleate and sodium stearate in nujol were determined as follows: A thermometer was introduced in the centre of the test tube (2.6 cm. diam.) containing the gel forming mixture, after the condensing column was removed and the tube was placed in a thermostat maintained at a constant temperature. A stop-watch was started immediately and the temperature of the gel-forming solution was noted at definite intervals of time (15

seconds). In order to obtain strictly comparable results with the solvent it was also heated in the same test tube to the same temperature as the solution and was allowed to cool in the thermostat maintained at the same temperature. Some of the results obtained are graphically represented in Figs. 1 and 2

FIG. 1

Sodium oleate in nujol. ($T=50°$).



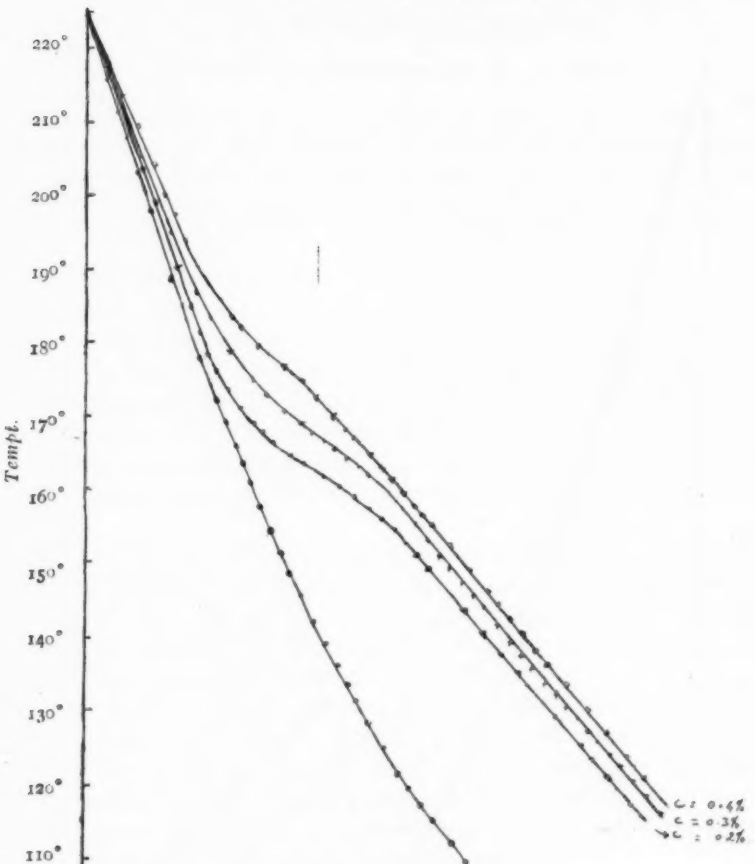
DISCUSSION

It can be seen that (*i*) up to a certain stage the cooling curves for solutions coincide more or less with those of the solvents and after this stage the solvents cool faster

than the solutions under identical conditions of cooling, and (*ii*) the higher the concentration of the soap, the slower is the rate of cooling of the solutions.

FIG. 2

Sodium stearate in nujol ($T=50°$).



The curves for solutions show that they change their directions at two points in each curve, thus furnishing a kink in the curves. This indicates that heat is evolved during this stage. The time of setting determined by Flemming's method occurs during the range of the kink. This establishes that heat is evolved during the sol-gel transformation.

The evolution of heat can be explained on the basis of the theory of gel-formation. The soap particles in soap solutions are more or less in a molecular state and possess a definite amount of kinetic energy. On cooling, the solution undergoes saturation and supersaturation, which lead to the formation of colloid particles and their final agglomeration to the gel state. In this process a restriction would be imposed on the degree of freedom of motion of individual particles, which would lead to the reduction of kinetic energy ; this is given out as heat of gelation.

The actual amount of the heat of gelation (H) has been calculated in each case from the relation,

$$H = \frac{S_1\theta_1 + S_2\theta_2}{2} \times t,$$

where S_1 and S_2 are the specific heats in the sol and the gel states, θ_1 and θ_2 are their respective rates of cooling and t, the time in seconds over which heat is evolved. The results obtained are recorded in Tables I and II. The results confirm that (*i*) for any one concentration of the soap, the specific heat in the sol state is greater than that in the gel state and (*ii*) the specific heats in the sol and the gel states of the same system increase with the increase in concentration of the soaps. Further, it will be observed that the heat of gelation increases as the soap content is increased. Also the heat of gelation of a system of a particular concentration is almost independent of the rate of cooling, that is, of the temperature of surroundings.

TABLE I

Sodium oleate in nujol.

C.	T.	S_1.	S_2.	H.	T_g+273.	MH.	$\frac{MH}{T_g+273}$.
0.2	40°	1.5	1.3	29.14	412	44350	105.0
0.3	40°	1.8	1.5	42.72	423	43350	102.5
0.5	40°	2.1	1.6	67.96	428	41390	96.7
0.2	50°	1.6	1.3	28.62	412	43580	103.3
0.3	50°	2.0	1.6	40.10	423	40660	96.1
0.5	50°	2.2	1.7	70.30	428	42800	100.0
0.2	60°	1.7	1.4	28.30	412	42024	102.0
0.3	60°	2.0	1.7	40.00	423	40500	98.8
0.5	60°	2.3	1.7	67.63	428	41180	96.2

An interesting point is observed when the values of the ratio of the heat of gelation per gram molecule of soap to the temperature of setting in absolute units, recorded in the last column of Tables I and II, are examined. It will be seen that for the same system these are very nearly constant. Also there appears to be a vague similarity between these results and Trouton's rule, a generalisation according to which the ratio of the molar latent heat of vaporisation to the boiling point is constant for most substances.

TABLE II

Sodium stearate in nujol.

C.	T.	S_1.	S_2.	H.	T_g+273.	MH.	$\frac{MH}{T_g+273}$.
0.2	40°	1.8	1.3	27.24	425 0	41680	98.1
0.3	40°	2.0	1.6	43 30	432.0	43860	100.5
0 4	40°	2.1	1.6	59.98	436.5	46350	106.2
0.2	50°	2.1	1.4	28.28	425.0	43140	101.5
0.3	50°	2.1	1.7	43.66	432 0	45570	105 5
0.4	50°	2.2	1.7	58.79	436.5	44970	103.0
0.2	60°	2.2	1.9	28.67	425.0	46920	100.4
0.3	60°	2.3	1.8	40.64	432.0	42420	98.2
0 4	60°	2.3	2.0	56 19	436.4	43840	100.4

One more striking observation that can be made on close examination of the curves is that in all the cases, the point of setting of the system of a gel, determined for a particular concentration by an independent method, lies in the middle or the end portion of the kink. This can be explained as follows: The thermometer records the temperature at the centre of the system which is higher than the temperature of the outermost layers in contact with the surrounding. This gives rise to a temperature gradient within the system, varying from the temperature recorded at the centre to the temperature of the surrounding. The gelation takes place in layers, and the heat of gelation evolved by the outermost layers retards the rate of cooling of the inner layers. Hence, the changes in direction of the curves at this stage are gradual. In the light of these observations, the setting point should lie at the end of the kink. However, this has not been realised because the setting observed by the inversion of the tube may be due to the setting of most of the outer layers and not necessarily of the entire systems.

The authors express their sincere thanks to Dr. Mata Prasad, D.Sc., F.N.I., F.R.I.C., for suggesting the problem and for guidance.

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A NOTE ON THE OCCURRENCE OF "CERYL ALCOHOL" IN *ARGEMONE MEXICANA*

By Brojeswar Majumder, Sachindra Nath Sarkar and Phanindra Chandra Dutta

Argemone oil, extracted from the seeds of *Argemone mexicana*, received considerable attention because of its extensive use in adulterating mustard oil and of its etiological role in epidemic dropsy (Sarkar, *Ind. Med. Gaz.*, 1926, **61**, 62; Lal *et al.*, *Ind. J. Med. Res.*, 1939, **27**, 107; 1942, **30**, 145; Chopra *et al.*, *ibid.*, 1939, **27**, 947). From the seed-oil, Sarkar (*Nature*, 1948, **162**, 265) isolated two alkaloids, one of which had been identified with dihydrosanguinarine, described earlier by Späth, and the other, with sanguinarine. The toxic properties of the oil have been ascribed to these alkaloids. It became of interest to us to study the whole plant after carefully removing the seeds. Investigations on the whole plant were first reported by Schottenberg (*J. Amer. Chem. Soc.*, 1902, **24**, 238) and later on by Santos and Adkelen (*ibid.*, 1932, **54**, 2923). The latter group of workers have isolated two alkaloids, protopine and berberine from the Philippine varieties. Chemical examination of the whole plant *Argemone mexicana* of Indian origin was consequently undertaken to find out whether sanguinarine or its dihydro derivative could also be isolated. We have, however, substantiated the observations of Santos and Adkelen, and no other alkaloidal constituent could be detected in the plant.

From the non-nitrogenous fraction, we have isolated a highly crystalline compound, melting at 81°. Analytical data and other physical properties indicate that it is ceryl alcohol. It occurs widely in plant waxes (Pollard, Chibnall and Piper, *Biochem. J.*, 1931, **25**, 2111) and in insect waxes (Chibnall *et al.*, *ibid.*, 1934, **28**, 2196). The infra-red studies of the compound indicate the presence of a weak hydroxyl band and the absence of any other functional group in the molecule. It has been reported that ceryl alcohol is mainly *n*-hexacosanol (Bill and Steel, *Proc. Exp. Biol. Med.*, 1933, **31**, 134) but the presence in small amount of primary alcohols having close molecular weights has also been confirmed in ceryl alcohol (Chibnall *et al.*, *loc. cit.*). It has no toxic properties and has no feeding value and it is excreted unchanged from animal system.

While investigating other plants of medicinal value in the Organic Laboratories of the Indian Association for the Cultivation of Science, Dr. A. K. Mitra has isolated 'ceryl alcohol' from the leaves of *Zizyphus jujuba lomk*, Rhamineae, in a yield of 0.2%, in addition to other products.

The plants were collected just before the flowering stage. The whole plant was dried in the shade and finely ground. Next it was extracted in a Soxhlet with rectified spirit containing acetic acid (5%). The extract was next concentrated. The dark-

coloured viscous residue was repeatedly washed with dilute hydrochloric acid to remove the alkaloids according to Santos and Adkelen (*loc. cit.*). The alkaloid fractions were separated into protopine (m.p. 206°) and berberine, the latter being characterised through tetrahydroberberine (m.p. 168°). The insoluble portion was washed with rectified spirit when the major portion of chlorophyll went into solution, and removed. The solid sticky residue was repeatedly washed with alcohol till a residue of light brown colour was obtained. This was repeatedly crystallised from acetone. The crystals were again dissolved in chloroform and passed through a column of aluminia when a colorless solution was obtained. On cooling the concentrated solution, rod-shaped crystals were obtained. From ethyl acetate it separated in hexagonal plates. (Found : C, 81.59, 81.71 ; H, 14.06, 13.04. Calc. for $C_{26}H_{34}O$: C, 81.6 ; H, 14.2 per cent).

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A NOTE ON BROMINATION OF OXYMETHYLENE KETONES THROUGH THEIR COPPER SALTS

By H. G. Garg, Y. Singh and M. M. Bokadia

Wislicenus and Ruthing (*Annalen*, 1912, **379**, 260) brominated oxymethylene-desoxybenzoin in glacial acetic acid. Deshapande *et al.* (this *Journal*, 1946, **23**, 43; 1949, **26**, 55) effected the bromination of oxymethylene-*cyclo*hexanone and oxymethylene-methyl-ethyl ketone in the same way. Brühl (*Ber.*, 1904, **37**, 2175, 2176) obtained bromo-oxymethylene-menthone and bromo-oxymethylene-camphor by adding bromine to the oxymethylene ketones, neutralised with caustic soda. Deshapande *et al.* (*loc. cit.*) obtained bromo-oxymethylene-acetophenone by the bromination of the sodium compound of oxymethylene-acetophenone in dry carbon tetrachloride.

We brominated oxymethylene-methyl-*n*-amyl ketone, oxymethylene-acetophenone and oxymethylene-camphor through their copper chelate compounds in an inert solvent. This method provides a better yield of the purer product, and the copper salt can be preserved easily. The copper salt method has been used in the preparation of αγ-dibromoethyl acetoacetate from γ-bromoethyl acetoacetate. Although bromination of oxymethylene-methyl-*n*-amyl ketone has also been effected in ethereal solution, the copper salt method is found to yield better results.

*Bromination of Oxymethylene-methyl-*n*-amyl Ketone.*—Oxymethylne-methyl-*n*-amyl ketone (4 g.) (Bokadia and Deshapande, this *Journal*, 1953, **30**, 383) was shaken with a saturated solution of aqueous copper acetate, forming a greenish blue copper salt, m.p. 130°. The copper salt was suspended in dry ether and to this bromine (2 *M*), suspended in dry ether, was added gradually with constant shaking in the cold. The copper bromide formed was removed by filtration. The filtrate on evaporation afforded a gummy mass, which on crystallisation from petroleum ether furnished a white solid, m.p. 69°, yield 1 g. It develops a violet colour with ferric chloride solution. (Found : Br, 36.2. $C_8H_{13}O_2Br$ requires Br, 36.9 per cent).

*Bromo-oxymethylene-methyl-*n*-amyl Ketone from the Oxymethylene Ketone.*—Oxymethylene-methyl-*n*-amyl ketone (2 g.) was dissolved in dry ether and to this bromine (1 *M*), suspended in dry ether, was added gradually in the cold. The solution on evaporation in cold gave the bromo derivative, m.p. 69°, after crystallisation. But the yield (0.2 g.) in this case was poor.

Bromo-oxymethylene-acetophenone. — The copper salt of oxymethylene-acetophenone (5 g.) was brominated, as described above, in dry CCl_4. The solid product (yield 3 g.) on recrystallisation from acetic acid melted at 106° (cf. Deshapande *et al.*, *loc. cit.*).

Bromination of d-*Oxymethylene-camphor.*—The crude copper salt of *d*-oxymethylene-camphor (m.p. 160°, 2.5 g.) was brominated in the same way as before. Bromo-oxymethylene-camphor (yield 2.5 g.) after crystallisation from alcohol melted at 43° (cf. Aschan, *Ber.*, 1894, **27**, 2398 ; Brühl, *Ber.*, 1904, **37**, 746, 759 ; Fjader, *Chem. Zentrl.*, 1933, II, 51).

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A NOTE ON THE OXIDATION OF RED PHOSPHORUS BY POTASSIUM CHLORATE

By G. S. Deshmukh and M. Venugopalan

The qualitative aspect of the oxidation of phosphorus by potassium chlorate has been studied by many workers (Bottger, *Rep. Pharm.*, 1875, **24**, 725; Slater, *J. prakt. Chem.*, 1853, *i*, **60**, 274; Schrotter, *Sitzber. Akad. Wien*, 1848, **1**, 130) who have shown that phosphorus and phosphoric acids are formed as the end products. During studies in these laboratories on the quantitative aspect of the above oxidation process, their reaction was found to be rather complicated, and conditions determining the reaction in some particular phase were studied.

The decomposition of $KClO_3$ as $KClO_3 \longrightarrow KCl + 3O$ and the utility of the three atoms of oxygen for the oxidation of P to phosphoric acid have been studied in solutions containing sulphuric acid of 1*N* (overall *N* being $\ll$ 1 *N*-H_2SO_4). The reaction is represented by

$$6P + 5KClO_3 + 9H_2O \longrightarrow 6H_3PO_4 + 5KCl.$$

Thus, it was found that 6 molecules of P would require 5 of $KClO_3$ for quantitative oxidation on the basis of the above reaction. Apart from these considerations, complete and quantitative oxidation was invariably impracticable; but from the results, the percentage of oxidation could be evaluated.

Procedure.—A known quantity of pure dry red P was weighed into a Kjeldhal flask provided with a Liebig condenser attached with a ground glass seal. About 5 to 10 times (the weight of P taken) pure Merck's sample of potassium chlorate was tapped into the flask and 40 c.c. of *N*-H_2SO_4 was added and the whole system refluxed for about 6 to 8 hours by direct heating. On completion of the reaction, the flask was cooled and the remaining solution of excess chlorate made up to 250 c.c., 50 c.c. of which was pipetted into a conical flask and an excess of ferrous ammonium sulphate solution (50 c.c. of *N*/10) was added to it, followed by dilute H_2SO_4. The flask was fitted up with a cork provided with a Bunsen type of valve tube and the contents boiled. It was cooled and the excess ferrous sulphate titrated against $KMnO_4$ solution.

The above experiments were repeated in the presence of a catalyst, viz., manganous sulphate. To the contents in the flask about 5, 10, 15 and 20 c.c. of an 1% solution of Merck's manganous sulphate was added prior to refluxing, and experiments carried out. A few of the results are shown in Table I.

TABLE I

Overall acidity $\ll$ 1N-H_2SO_4.

P taken.	$KClO_3$.	Catalyst (1% $MnSO_4$).	Unchanged $KClO_3$.	Changed $KClO_3$.	P (calc.).	Diff.
0.0212 g.	0.2720 g.	...	0.2046 g.	0.0674 g.	0.02047 g.	0.00073 g.
0.0336	0.2720	...	0.1741	0.0979	0.02971	0.00389
0.0338	0.2958	...	0 1941	0.1017	0 03085	0 00295
0 0132	0.2958	5 c c.	0.2532	0.0426	0.01293	0.00027
0.0400	0 2958	10	0.1751	0.1207	0 03662	0.00338
0.0426	0.2958	15	0.1680	0.1278	0.03877	0 00383
0.0290	0.2958	20	0.2053	0.0905	0.02746	0.00154

The results show the erratic behaviour of the oxidant in the reaction. Also the results obtained by back-titration of chlorate were slightly variable from that obtained by titrating the chloride formed in solution by the Volhard method.

Accuracy of the method has been found to vary from 2 to 10% negative error, for P ranging from 0.02 to 0.04 g. and hence 90% of red P goes to complete oxidation. Manganous sulphate catalysed the reaction to some extent, for it was observed that more of P was oxidised to phosphoric acid in the same time.

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A NOTE ON COMPONENT FATTY ACIDS OF THE OIL FROM THE SEED OF *MOMORDICA CHARANTIA*, LINN.

By J. P. Verma and J. S. Aggarwal

Momordica charantia, Linn. (Hindi : Karela) belongs to N.O. Cucurbitaceae. Airan and Shah (*J. Univ. Bombay*, 1942, **11**, 105) reported the fatty acid composition of the seed oil as stearic and oleic acids. As the oil polymerises and gels quickly, Aggarwal (Proc. Sym. Oils Fats & their Utilization, N.C.L, Poona, 1951, p. 257) suspected the presence of a conjugated double bond fatty acid in its composition. The work carried out to determine the fatty acid composition of the oil from the Bombay variety of karela seeds by applying the low-temperature crystallisation and spectroscopic techniques has been summarised in this note. When the work was nearing completion, Chowdhury, Chakrabarty and Mukherji (*Proc. Indian Sci. Cong.*, 1955, Part III, 156) reported the fatty acid composition of the seed oils from two Bengal varieties of *Momordica charantia*.

The karela seeds, on extraction with petroleum ether, yield 26.5% of a clear reddish brown oil having the characteristics: d^{40}, 0.9958 ; n_D^{37}, 1.4984 ; acid value, 3.4 ; sapon. value, 184.1 ; I.V. (Wijs, 2 hrs), 120.4 ; I.V. (R & K modified method), 196.5 ; Diene value (Ellis & Jones), 70.6 ; saturated acids, 28.0 ; unsaponifiable matter, 0.7%.

The fatty acids (100 g.), prepared from the oil by the usual saponification method in the atmosphere of nitrogen, were dissolved in 1000 c.c. of petroleum ether (b.p. 40°-60°) and separated into four fractions by low-temperature crystallisation at 0°, -15° and -25°. The material (20.6 g.) separating at -25° was crystallised from methyl alcohol (90%) by warming at 35°-40° and keeping at 15° when α-elaeostearic acid [m.p. 47-48° ; I.V. (R & K), 245 ; M.W., 279.1 ; $E_{1cm}^{1p.c.}$ value at 268-70 mμ, 1780] was obtained. The acid on irradiation in ultraviolet light in petroleum ether in presence of traces of iodine changed into its β-isomer, m.p. 70-71°.

The α-elaeostearic and linoleic acids in the total fatty acids of the oil from the seeds of *Momordica charantia* were estimated by the ultraviolet spectroscopic method, as reported by Hilditch, Morton and Riley (*Analyst*, 1945, **70**, 68). The procedure also indicated the complete absence of linoleic acid. The saturated acids, obtained after Bertram's permanganate oxidation method of total fatty acid mixture, amounted to 29.8%, having the mean M.W. 285.4. After recrystallisation from dilute alcohol, the specimen melted at 70° which remained unchanged on admixture with an authentic specimen of stearic acid (m.p. 70°-70.5° ; M.W. 284.5). The saturated acids therefore were entirely stearic acid. The total of saturated, elaeostearic and linoleic acids, when subtracted from 100, gave the amount of oleic acid. The presence of linoleic and oleic acids in total fatty acids was confirmed by the isolation of tetrahydroxystearic acid (m.p. 155-56°) and dihydroxystearic acid (m.p. 130-31°) from the alkaline

potassium permanganate oxidation products of the petroleum ether concentrate obtained after removal of the α-elaeostearic acid at -25° (Sullivan and Bailey, *J. Amer. Chem. Soc.*, 1936, **58**, 383).

The fatty acid composition of the oil from the seeds of *Momordica charantia*, Linn. (karela), as obtained by the above analysis, is α-elaeostearic acid, 46.7% ; linoleic acid, 7.7% ; oleic acid, 15.8% and stearic acid, 29.8%.

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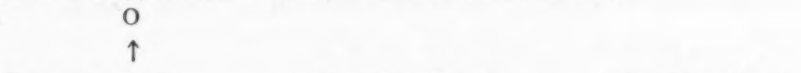
A NOTE ON THE STRUCTURE OF DISULPHOXIDES

By B. N. Trivedi

Constitution of disulphoxides has been a subject of some interest. Mainly structures (I), (II) and (III) appear to have been discussed for these substances:

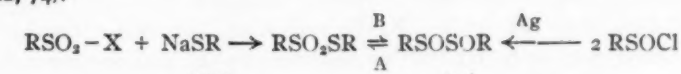


(I) (II) (III)

The structure (I) has been considered unlikely in view of the formation of these substances from sulphonyl halides in which the structure $R—SO_2—X$ is unquestioned. The structure (II) has received some support from measurements of optical rotatory power of certain of these compounds (Hilditch, *J. Chem. Soc.*, 1910, **97**, 1091; Toennies and Lavine, *J. Biol. Chem.*, 1936, **113**, 571, 583). But their usual reactions are best explained on the unsymmetrical structure—thiosulphonate (III)—and the work of Smiles *et al.* (*J. Chem. Soc.*, 1924, 176; 1925, 224) would appear to have finally settled the issue in favour of this. These workers have further shown that in compounds, where R and R′ are different, isomeric products having both the oxygens attached to one or the other of the sulphur atom are formed, and these isomers are not mutually interconvertible.

Through a series of changes, detailed below, we have now synthesised a few disulphoxides where the symmetrical structure (II) must be assumed. Since these compounds are identical in all respects with the corresponding thiosulphonates (III), already known, it will not be unreasonable to conclude that one of the following isomeric changes (A) or (B), most probably (B), must be taking place during the process of synthesis of these compounds.

The decomposition of a symmetrical structure into unsymmetrical products (as shown by Smiles *et al.*, *loc.cit.*) is not unusual in the chemistry of sulphur-oxygen compounds. For example, the salts of dithionous acid decompose to sulphur and a sulphite, although there is undisputable evidence for a symmetrical structure for this compound (*Curr. Sci.*, 1953, **22**, 74).



(III) (II)

The sulphonyl chlorides, the starting materials, were prepared by the action of PCl_5 on the alkali sulphonates or by the chlorsulphonation of the appropriate hydrocarbon. These on reduction with zinc and alcohol furnished the corresponding sulphinic acids which by the action of thionyl chloride were converted into the corresponding sulphinyl chlorides, RSOCl. The sulphinyl chlorides in dry petroleum ether reacted with finely divided silver leaf and afforded the appropriate disulphoxides. A summary of the results is presented in Table I.

TABLE I

Disulphoxide prepared.	M.P.		% Sulphur.		Mol. wt.	
	Found.	Authentic.	Found.	Calc.	Found.	Calc.
1. ββ′-Dinaphthyl	106-108°	106-108° *	17.80 17.84	18.2	350	385
2. pp′-Ditolyl	76-77°	76° **	22.9 22.7	23.0	272	278
3. 4:4′-Dichlorodiphenyl	136 38°	136-38° †	19.7 19.5	20.0	312	319
4. 4:4′-Dibromodiphenyl	159-60°		15 21	15.6	414	408

* Otto, Rossing and Troeger, *J. prakt. Chem.*, 1893, **47**, 97.

** Otto and Gruhm, *Annalen*, 1868, **145**, 13.

† Otto, *ibid.*, 1868, **145**, 323.

ββ′-Dinaphthyl Disulphoxide.—β-Naphthalenesulphonyl chloride and β-naphthalenesulphinic acid were prepared by the methods of Erdmann (*Annalen*, 1893, **275**, 233), Krafft and Roos (*Ber.*, 1892, **25**, 2261) and Otto and Rossing (*loc.cit.*) respectively. The dry sulphinic acid on treatment with excess of thionyl chloride afforded the β-naphthalenesulphinyl chloride (cf. Hilditch and Smiles, *Ber.*, 1908, **41**, 4113), m.p. 96-98°. (Found : Cl, 16.46, 16.50 ; S, 15.6. Calc. for $C_{10}H_7OClS$: Cl, 16.84 ; S, 15.2 per cent).

The well-dried sulphinyl chloride was treated in dry petroleum ether (b.p. 60°-80°) with excess of fine silver leaf for 8 hours at 60°-65°. The residue, left on evaporation of the petroleum ether under reduced pressure, was crystallised from absolute alcohol, m.p. 106-108° (cf. Otto, Rossing and Troeger, *loc.cit.*). Sulphur was estimated and the molecular weight in benzene determined by Beckmann's method (Table I).

pp′-*Ditolyl Disulphoxide.*—*p*-Toluenesulphonyl chloride and *p*-toluenesulphinic acid were prepared by the method of Bourgeois (*Ber.*, 1885, **18**, 436), Krafft and Roos (*loc.cit.* p. 2259), and Graber (*Ber.*, 1876, **9**, 1586 ; *Annalen*, 1867, **142**, 95) respectively. The corresponding sulphinyl chloride was prepared by the action of thionyl chloride (Hilditch, *loc.cit.*). The dry sulphinyl chloride in petroleum ether, when treated with excess of fine silver leaf, furnished the *pp′*-ditolyl disulphoxide (*vide supra*), m.p. 76-77° (Lowenthal and Graber, *Annalen*, 1869, **149**, 102). Sulphur and molecular weight in benzene were determined (Table I).

4:4′-*Dichloro and* 4:4′-*Dibromo Disulphoxides.*—*p*-Halobenzenesulphonyl chlorides and the corresponding sulphinic acids were prepared (Ullmann *et al.*, *Ber.*, 1907, **40**, 642 ; Gattermann, *Ber.*, 1899, **32**, 1142 ; Krafft and Roos, *loc. cit.*). The latter on treatment with thionyl chloride by Hilditch's procedure gave the 4-halobenzenesulphinyl chlorides, which on prolonged treatment with excess of fine silver leaf in dry petroleum ether at 60-65° gave the 4:4′-dihalo disulphoxides (Otto, *loc. cit.*, p. 323). Further work is in progress.

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A NOTE ON THE SOLUBILITY OF HYDRATED COPPER OXIDE IN NITRIC ACID

By S. C. Sircar and B. Prasad

The value of solubility product of copper oxide, as calculated by Feitkmecht (*Chem. Abs.*, 1945, 856) is 1×10^{-20}. The above author has calculated it from thermal data, whereas Nasanen and Tamminen (*J. Amer. Chem. Soc.*, 1949, **71**, 1994) have determined it from a system of cupric oxide, cupric perchlorate and sodium perchlorate, and found the value as 2.2×10^{-20} and they claim that the cupric oxide is stable. Herein a simpler method has been adopted by the present authors.

Copper oxide, prepared from cupric chloride and caustic soda, was washed free of alkali and chloride, and dried over an electrically controlled air-oven at 110°-115° for 15 hours. The oxide was found to contain about 5% water.

A stock solution of nitric acid, standardised against borax, was kept for preparation of other solutions by dilution.

Dilute nitric acid of known strength was shaken with sufficient copper oxide for 8 days (6 days required for equilibrium). The undissolved copper oxide was removed by filtration in a G_4 glass sinterred crucible under pressure. The p_H of the filtrate was measured with a Marconi-p_H meter, and its copper content was estimated iodimetrically. The solid phase got hydrated to copper oxide of about 35% water content. This hydration did not materialy affect the concentration of acid. The experiments were carried out in triplicates at room temperature (25°-28°). A few sets of bottles were placed in a thermostat at 35°, but it was found that p_H or copper concentration did not change appreciably with temperature, proving the temperature coefficient to be small. The experimental results are shown in Table I.

Table I

Initial conc. of HNO_3.	Conc. of Cu.	p_H.	$a^2_{OH} \times 10^{12}$.	$a^2_{OH} \times a_{Cu^{++}} \times 10^{20}$.
0.0201 *M*	0.0100 *M*	5.28	37.03	1.9
0.0402	0.0200	5.20	25.63	2.3
0.0604	0.0301	5.11	16.92	1.9
0.0805	0.0384	5.02	11.19	1.5
0.1006	0.0482	4.95	8.102	1.6
0.1207	0.0580	4.84	4.882	0.8
0.1408	0.0676	4.74	3.080	0.6

Mean value: 1.5×10^{-20}.

The total concentration of copper ([Cu]) in the solution can be represented as :

$$[Cu] = [Cu^{2+}] + [CuO] + [Cu(NO_3)_2]$$

where $[Cu^{2+}]$, [CuO] and $[Cu(NO_3)_2]$ represent the copper ion concentration, copper oxide concentration and undissociated copper nitrate concentration respectively. The

solubility of copper oxide has been reported by McDowell and Johnston (*J. Amer. Chem. Soc.*, 1936, **58** 2009) as 3×10^{-5} mole of copper oxide per litre and so can be neglected. The work of Sidgwick and Tizzard (*J. Chem. Soc.*, 1908, **93**, 187) on colour and concentration of copper salts leads to the complete dissociation of copper nitrate within this range of concentration. So it becomes evident that copper remaining in these two forms is not of any importance, and the total copper can be assumed to exist as Cu^{2+} ion. From the knowledge of p_H and the concentration of copper in the solution, it is possible to calculate the thermodynamic solubility product. The activity coefficient of copper has been calculated on the same principle as on bi-monovalent salts (this *Journal*, 1952, **29**, 169). The mean value of the solubility product of copper oxide comes out to be 1.5×10^{-20}.

The solubility product determined by us as well as by previous authors corresponds to the following equilibrium :

$$CuO, nH_2O + H_2O \rightleftharpoons Cu^{2+} + 2OH^- + nH_2O$$

and not to the equilibrium

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-.$$

The solubility product corresponding to the two equilibria should be as follows

$$(1)\quad K_{sp} = \exp.\frac{\mu_{CuO,\,nH_2O} - (n-1)\,\mu_{H_2O} - \mu^\circ_{Cu^{2+}} - 2\mu^\circ_{OH^-}}{RT}$$

$$(2)\quad K_{sp} = \exp.\frac{\mu_{Cu(OH)_2} - \mu^\circ_{Cu^{2+}} 2\mu^\circ_{OH^-}}{RT}$$

Our value, which corresponds to the first equilibrium, is in fair agreement with those of previous authors, referred to earlier. The solubility product (2.6×10^{-19}) corresponding to the second equilibrium has been determined by Nasanen (*Ann. Acad. Sci. Fennicae*, A. 597, 1942).

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REVIEWS

The Relaxation Behaviour of Matter: Addresses & Discussions of the 2nd Marburg Conference, 1953. Reprinted from *Koll. Zeit.*, Vol. 134. Edited by Prof. Dr. F. Horst Müller, Marburg, Lahn.

This discussion is the second, held at Marburg (Oct. 2nd - Oct. 4th, 1953). The first one was on the solid state of highpolymer substances, held in 1950.

The electrical after-effect and dielectric dispersion are classical examples of the time lag in certain equilibrium phenomena in the macroscopic behaviour of matter. Introducing the Discussion, Dr. Welcher very rightly said, "Relaxation phenomena play a great role in the most varied branches of Physics and Physical chemistry and each branch has developed its own ideas and formulations Prof. Müller has done therefore an immense service to science by bringing these various disciplines, which are parts of a whole, into a discussion group".

The paper by Prof. J. Meixner on the thermodynamic theory of relaxation phenomena and its relation to the 'after-effect' theory (Nachwirkungstheorie) clarifies the formalism and general laws of thermodynamic relaxation. He shows how the thermodynamic functions for the false equilibrium can be calculated by means of statistical mechanics. The derivation of phenomenological coefficient is difficult and can be made from quantum mechanical considerations. He refers to the possibility of a thermodynamic resonance relaxation. On this basis, as Prof. Meixner says, a comprehensive theory of the elastic relaxation of isotropic and anisotropic bodies and of dielectric and magnetic relaxation of substances can be developed.

Prof. Kneser's paper on mechanical relaxation gives a clear presentation of the theory and experimental results of simple systems selected from gas, liquid and solids. He classifies various relaxation phenomena into three categories: Temperature relaxation, Structure or Pressure relaxation and Orientation or Entropy relaxation, and discusses them with typical examples from the gaseous, liquid and solid systems.

The paper on Paramagnetic relaxation by Van der Marel gives a short review of the theory and experiments pertaining to it and the experimental measurements made by him with paramagnetic and non-paramagnetic salts. Ferromagnetic relaxation phenomena in α-iron and highly permeable ferites are discussed by Mr. Feldtkeller.

Dr. Jenckel's attempt to understand the plastic-elastic behaviour by means of models in which the elastic part is represented by a fibre and the viscose part by a bulb moving in a cylinder, depicts a clear picture, although of a qualitative nature, of the mechanical behaviour of substances.

In the visco-elastic processes two functions play a fundamental role — the 'Kriech' curve and the Relaxation curve. The simple theory leads to an exponential expression, but a closer study leads to two distribution functions, relaxation spectra as they are called, which can interpret both the curves. The theoretical aspects of the problem and the physical significance of the relaxation spectra and their evaluation in terms of

experimental measurements are discussed in two papers by Prof. Gross, followed by an elaborate analysis, particularly of the temperature and frequency dispersion and the principle of superposition by Prof. Müller.

The experimental results of dielectric dispersion of a number of substances including high polymers are discussed by Brot, Magat and Reinsh and by Würstlin. The relation of mechanical relaxation phenomena of high polymers to their structure is exemplified by the studies reported by Schmeider and Wolf, in which they describe the torsional modulus and logarithmic decrement of mechanical damping as a function of temperature.

The statistical mechanical approach to understand relaxation of matter on the basis of theory of fluctuation has been attempted by Kubat and Müller.

The interesting discussions at the end of each paper are exceedingly useful and thought provoking. Those who are interested in the problem of relaxation of matter and its present position will find the volume very helpful and stimulating.

S. K. M.

OBITUARY

Mme Irene Joliot-Curie

(1897-1956)

The death of Mme Irene Joliot-Curie in a Paris hospital on March 17, 1956, has removed a towering figure from the world of science. She with her husband, Prof. Frederic Joliot-Curie, repeated the achievements of her illustrious parents, Mme Curie and Pierre Curie, of undying fame and romantic career. While the latter, by their epoch-making discovery of radium and its remarkable properties, laid the foundation of a new branch of science, radioactivity, which overturned many cherished conceptions and provided means for the exploration of the structure and the constitution of atoms, the couple Joliot-Curie distinguished themselves by proceeding a step further with their discovery of induced radioactivity. This prepared the ground for the building up of another new and fascinating branch of science, known as nuclear physics and nuclear chemistry, which has opened up the way for the development of atomic energy and atomic bombs, and ushered in an era of great hope as also of greater horror for the future of humanity. Like her parents again, she and her husband achieved the highest distinction for a scientist by winning the Nobel Prize for Chemistry in 1935. This is indeed an instance of what may be said, history repeats itself.

Born in September 12, 1897, in Paris, Irene Curie was brought up in an atmosphere permeated with the spirit of highly intellectual and scientific culture. While still a child of 8 or 9 years she lost her father in that tragic street accident which has now become an almost historical event. Her education and training at this age were practically conducted by her grand-father Dr. Eugene Curie, who introduced her to natural history and botany, and moulded her character in no small measure. The spiritual equilibrium of Irene Curie in later life, her human sympathy, her political ideas, and her realistic attitude of mind may all be traced to the influence of her grand-father in her childhood. Besides, she had the rare benefit of that "collective teaching" which the brilliant luminaries of the University of Sorbonne, including her mother Mme Curie, organised for their own children. Instructions in every branch of science were thus imparted to these young people by a master-mind in the subject. Mme Curie gave them lessons in the most elementary course in physics. These lessons were often accompanied by experimental illustrations. The little pupils themselves were permitted to manipulate apparatus, to engage in experiments for their construction and even to try some reactions. Love of science and taste for experimental work were thus inculcated into the

mind of Irene, while still a young child. All these helped to polarise her intellectual life into a scientific career, dealing particularly with the study of that mysterious and marvellous element radium, the discovery of which brought unbounded fame and unstinted admiration to her parents from all over the world. After completing her secondary education at the College Sevigne, Irene joined the Radium Institute as an assistant, and started research work in radioactivity under her mother's guidance. During the World War I, while still a girl of seventeen, she used to take an active part in the work of her mother, who organised and directed the French Radiological Service. In discharging her duties in this sphere Irene had often to visit the field hospitals and stay in the army zones near the firing lines.

At the Institute of Radium, Irene found a young companion, Frederic Joliot, the most brilliant and high-spirited of the students. They often worked on the same problem. The partnership in scientific work soon matured into their partnership in life, and they were married in 1926.

The great work, by which Irene and Joliot repeated the achievements of her parents and acquired celebrity in the scientific world, is the discovery of induced or artificial radioactivity. In course of their study on the production of positrons by the bombardment of light elements like boron and aluminium, they found in 1934 that the emission of positrons continued for sometime even after removal of the source of the bombarding α-particles. The emission was found to decay following the well-known exponential law, valid in the case of naturally radioactive elements. The half-life period for the activated boron was 14 minutes and that for irradiated aluminium, 3.25 minutes. During the irradiation, however, they observed the expulsion of both neutrons and positrons. From this they came to the conclusion that a boron or an aluminium nucleus reacted with the α-particle, giving rise to an unstable or active isotope of another element with the liberation of a neutron. The active nuclei, thus produced, then undergo spontaneous disintegration with the emission of positrons, and behave, therefore, in this respect just like the naturally occurring radio-elements. These nuclear reactions may be represented by the equations:

$$_5B^{10} + {}_2He^4 \rightarrow {}_7{}^*N^{13} + {}_0n^1 \; : \; {}_7{}^*N^{13} \longrightarrow {}_6C^{13} + e^+$$

$$_{13}Al^{27} + {}_2He^4 \longrightarrow {}_{15}{}^*P^{30} + {}_0n^1 \; : \; {}_{15}{}^*P^{30} \longrightarrow {}_{14}Si^{30} + e^+$$

That boron gives an active isotope of nitrogen was shown by Curie and Joliot by irradiating boron nitride, BN, with α-particles, and then treating the substance with caustic alkali. An activity was detected in the evolved ammonia. In the case of irradiated aluminium the metal was dissolved in aqua regia to which sodium phosphate and a zirconium salt were added. The precipitate of zirconium phosphate showed the expected activity. The formation of radio-nitrogen and radio-phosphorus was thus conclusively demonstrated by usual chemical methods.

This was an outstanding discovery of great fundamental significance, which, as already stated, led to a revolutionary progress of science and technology. For this great work Irene Curie and her husband Joliot-Curie were awarded the Nobel Prize for chemistry in 1935, just within a year of her mother's death.

Mme Joliot-Curie visited India in 1950 with her husband as an overseas delegate to the Indian Science Congress Association, when she was awarded the Jay Kissen Mookherjee Gold Medal of the Indian Association for the Cultivation of Science in Calcutta. In 1949, on the occasion of the Silver Jubilee Celebration of the Indian Chemical Society, she was elected an Honorary Fellow of the Society. The Society has, therefore, special reason to share the general feeling of great loss the science has sustained by her death.

Mme Irene Joliot-Curie was an ardent pacifist with resolute courage. Her wide sympathy and liberal culture enabled her to view science with an unclouded and discerning vision against the background of human endeavour and human welfare.

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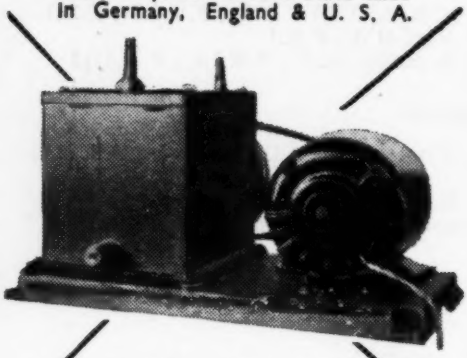

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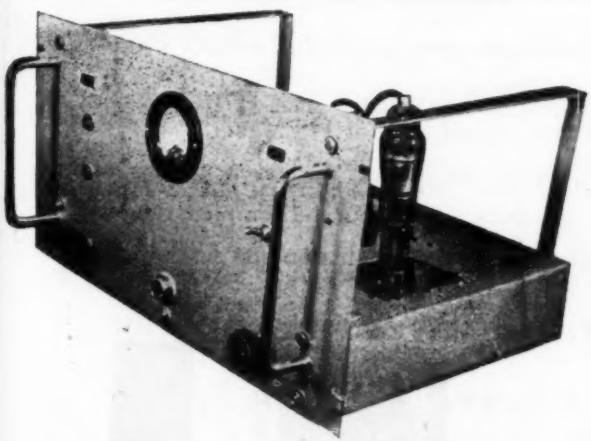

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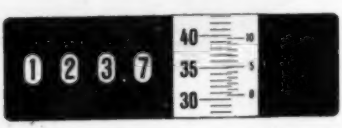

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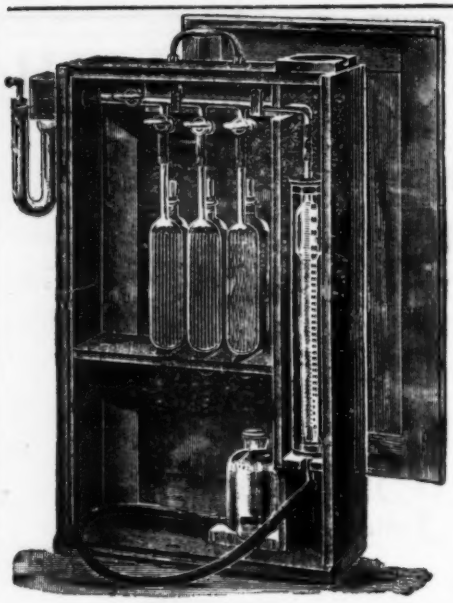

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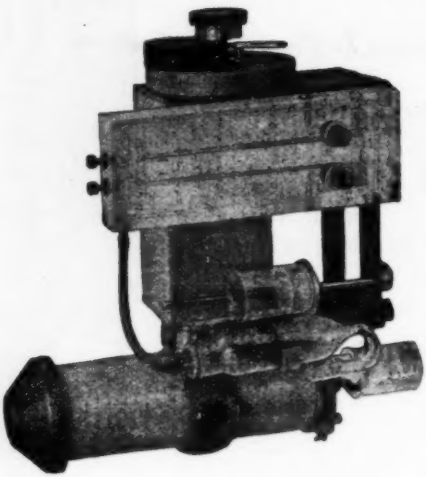

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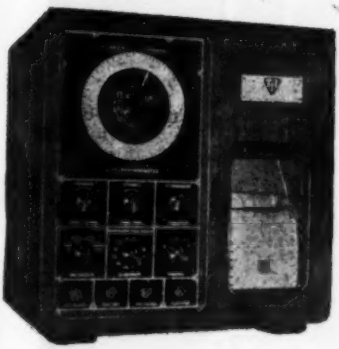

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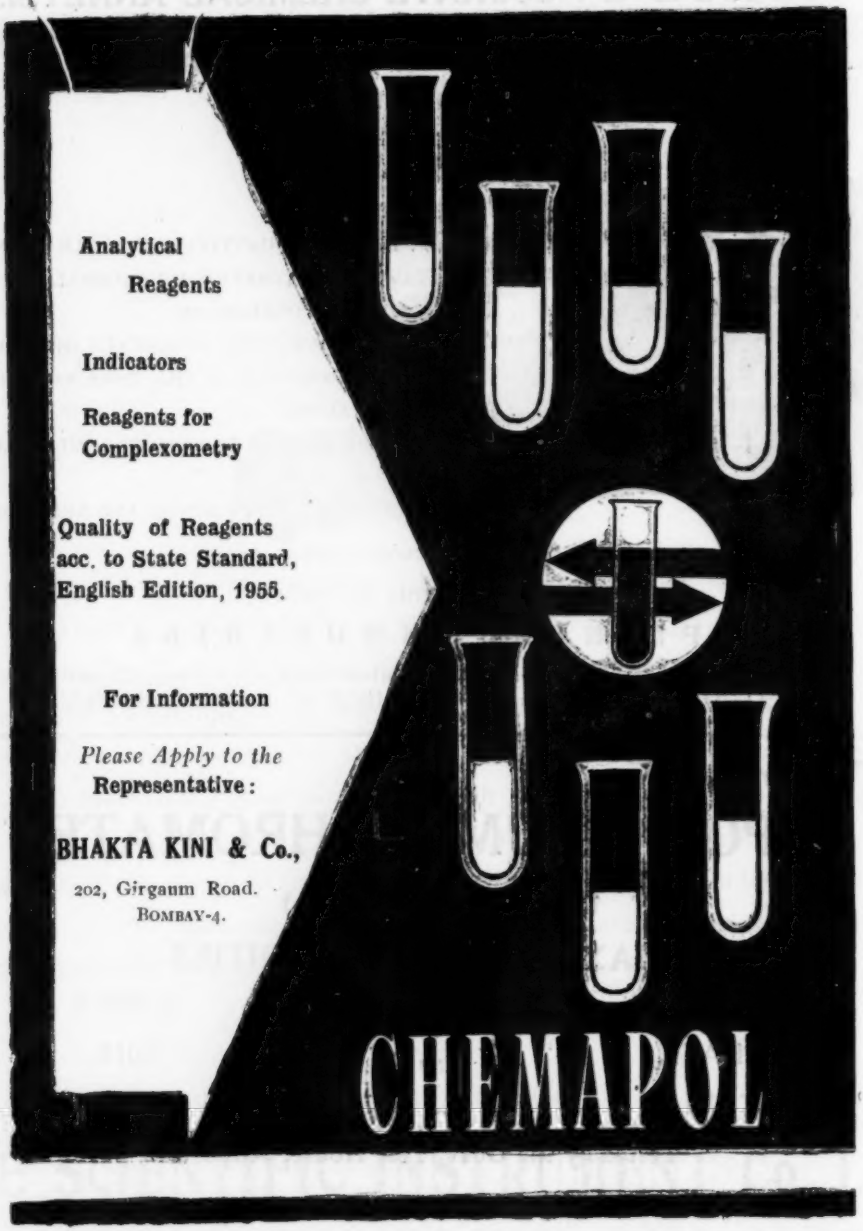

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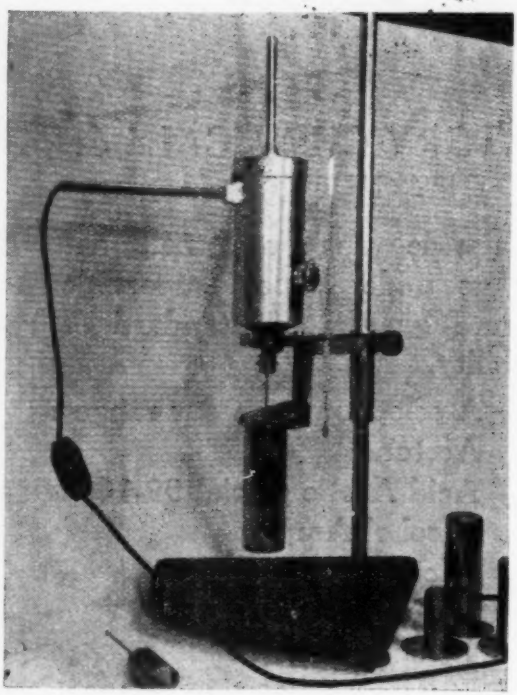

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